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SPECTROSCOPIC EVIDENCE OF THE B_2 MOLECULE AND DETERMINATION OF ITS STRUCTURE¹

By A. E. DOUGLAS² AND G. HERZBERG³

Abstract

In a discharge in helium with a trace of boron trichloride a new band system is found. The observation of isotope bands and in particular of an intensity alternation in the fine structure shows that the system is due to the diatomic boron molecule, B_2 . The B_2^{11} band heads are represented by the formula

$$\nu_H = 30546.1 + (929.3\nu' - 2.75\nu'^2) - (1035.2\nu'' - 9.58\nu''^2).$$

The bands consist of single R and P branches. The fine structure analysis yields the following rotational constants: $B_2' = 1.160$, $B_2'' = 1.212$, $\alpha' = 0.011$ and $\alpha'' = 0.014$ cm.⁻¹. From these the internuclear distances $r_2' = 1.625$ and $r_2'' = 1.590$ Å are obtained. It is shown that in all probability the system represents a $^2\Sigma_u^- - ^2\Sigma_g^-$ transition, the lower state being the ground state.

From the intensity alternation in the B_2^{11} bands, the spin of the B^{11} nuclei is found to be $5/2$. This value is in disagreement with recent theoretical predictions based on the Hartree as well as on the α -particle model of the nucleus.

Finally, a comparison with the other homonuclear diatomic molecules of the second period of the periodic system is made as well as a comparison of B_2 and C_2 with B_2H_6 and C_2H_6 .

Introduction

The ground state of the boron atom is a 2P state just as in the case of the fluorine atom. Therefore, according to the Heitler-London theory of homopolar valence, one would expect it to form a stable molecule with another boron atom. Also the Hund-Mulliken theory leads one to expect that B_2 is a stable molecule since in its ground state the difference between the number of bonding and anti-bonding electron pairs is $+1$ [see for example Herzberg (3)]. Finally the stability of diborane (B_2H_6) suggests that a stable bond between two boron atoms is possible. However, previous to our work (2), no evidence of the existence of diatomic B_2 had been obtained. Such evidence is of interest not only because of the confirmation of modern theories of valence it may supply and because it completes our knowledge of light diatomic molecules, but also for the reason that it makes possible a determination of the spin and statistics of the boron nuclei.

As is well known, boron has two isotopes, B^{10} and B^{11} , whose abundance ratio is about $1 : 4$. The B^{10} nucleus belongs to the rare class of nuclei with

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even mass number and odd atomic number of which the only known members are H^2 , Li^6 , B^{10} , N^{14} . The fact that N^{14} and H^2 follow Bose statistics and have integral spin ($I = 1$) was one of the main reasons for abandoning the idea of the presence of electrons in the nucleus in favour of the now current proton-neutron theory. For all nuclei other than H^2 , Li^6 , B^{10} , N^{14} the old and the new theory lead to the same conclusions as to whether the statistics is Bose or Fermi and whether the spin is integral or half-integral.

It would appear valuable to investigate spin and statistics in an additional critical case such as B^{10} . Also a knowledge of the spin of both B^{10} and B^{11} is necessary as a check on and a guide for the more detailed theories of nuclear structure.

From all these reasons a search for a spectrum of the B_2 molecule seemed important to us, and has been carried on at various times during the past 10 years. Recently we have been successful in finding a B_2 spectrum, and the following is a report on this work which establishes that the B_2 molecule is a stable molecule, determines its rotational, vibrational, and electronic structure, as well as its internuclear distance, and finally yields a value for the nuclear spin of B^{11} . It is hoped that in the near future it will be possible to determine also spin and statistics of B^{10} .

Experimental

Preliminary work with an electric arc between carbon electrodes filled with boron or boron carbide and run in an atmosphere of nitrogen, hydrogen, or helium did not lead to the observation of any new band system that might have been attributed to the B_2 molecule.

However bearing in mind that a discharge in helium to which a trace of another gas is added often brings out the spectrum of the latter better than a discharge in that gas alone, we tried a discharge in helium with a small amount of boron trichloride. The discharge tube had two hollow cylindrical aluminium electrodes co-axial with the straight Pyrex tube of 10 mm. diameter and 25 cm. length that carried the discharge. The tube was viewed end-on. It was run by a transformer supplying up to 8000 volts. The primary current varied from 12 to 15 amp. The helium used* contained a small trace of nitrogen, which fortunately disappeared after the discharge had been run for a little while. When this was established by the absence of the first positive group of nitrogen in the spectrum of the discharge as obtained with a pocket spectroscope, a small amount of boron trichloride was admitted. The colour of the discharge first turned from the yellow helium colour to a whitish-green which strongly exhibited the BCl spectrum. After a few minutes this colour gradually disappeared and the helium colour reappeared. Exposures taken just before the helium colour was completely restored showed a new band system that proved to be due to the B_2 molecule (see below).

* We are greatly indebted to Professors E. F. Burton and J. O. Wilhelm, McLennan Laboratory, Toronto, for supplying us with a tank of pure helium.

The exposures were taken with the new 20 ft. diffraction grating spectrograph of this department. In consequence of the mechanism of excitation (see above) plates could be exposed only for a few minutes at a time, after which fresh boron trichloride had to be admitted and the discharge had to be run until it almost disappeared before exposing again*. Fortunately the second order at 3000Å of our Wood grating was sufficiently bright that the total time for an exposure was not prohibitive (about one hour actual exposure time).

The plates were measured with a Gaertner comparator.

Vibrational Analysis

The band system that we found consists of two sequences as shown in Fig. 1, the stronger one being obviously the $\Delta v = 0$ sequence, the weaker one the $\Delta v = +1$ sequence. We have not been successful in obtaining further sequences because an increase in exposure time brings out a background that is partly due to BO (apparently produced by the action of atomic

TABLE I
DESLANDRES TABLE OF THE B_2 BANDS, GIVING HEADS AND ORIGINS FOR BOTH B_2^{11}
AND B_2^{10}

| $v' \backslash v''$ | 0 | 1 | 2 | 3 | |
|---------------------|--|-------------------------------------|-------------------------------|------------------------------|--|
| 0 | 30546.1 30518.10 — 30517.43 | | | | $\begin{matrix} \nu_H \\ \nu_o \end{matrix} \} B_2^{11} B_2^{11}$ $\begin{matrix} \nu_H \\ \nu_o \end{matrix} \} B_2^{10} B_2^{11}$ |
| 1 | 31472.7 31450.30 31495.8 31472.30 | 30447.2 30417.72 — — | | | $\begin{matrix} \nu_H \\ \nu_o \end{matrix} \} B_2^{11} B_2^{11}$ $\begin{matrix} \nu_H \\ \nu_o \end{matrix} \} B_2^{10} B_2^{11}$ |
| 2 | | 31368.0 31344.7† 31388.6 — | 30361.1 30330.8† — — | | $\begin{matrix} \nu_H \\ \nu_o \end{matrix} \} B_2^{11} B_2^{11}$ $\begin{matrix} \nu_H \\ \nu_o \end{matrix} \} B_2^{10} B_2^{11}$ |
| 3 | | | 31276.9 — 31296.0 — | 30290.1 — — — | $\begin{matrix} \nu_H \\ \nu_o \end{matrix} \} B_2^{11} B_2^{11}$ $\begin{matrix} \nu_H \\ \nu_o \end{matrix} \} B_2^{10} B_2^{11}$ |
| 4 | | | | 31200.2 — 31218.1 — | $\begin{matrix} \nu_H \\ \nu_o \end{matrix} \} B_2^{11} B_2^{11}$ $\begin{matrix} \nu_H \\ \nu_o \end{matrix} \} B_2^{10} B_2^{11}$ |

* We tried in vain to develop a continuous flow method.

† Calculated from band heads.

chlorine which releases oxygen from the glass) and partly to a continuum that always occurs when boron trichloride is present in a discharge. The above interpretation of the two sequences is confirmed by the observation of isotopic bands whose heads can be clearly seen in the $\Delta v = +1$ sequence (see Fig. 1). As usual for the $\Delta v = 0$ sequence, the isotope shift is too small to lead to separate heads.

Table I is the Deslandres table for the bands. It gives the wave numbers of the band heads for both $B^{11}B^{11}$ and $B^{11}B^{10}$, as well as the zero lines (band origins). The latter were determined directly from the branches for the bands whose fine structure was investigated. For the 2-1 and 2-2 bands they were obtained from the band heads by subtracting the theoretical distance between head and zero line as determined from the known or extrapolated rotational constants. For the remaining bands the zero lines are not given since the extrapolation of the rotational constants for them is too uncertain.

A formula of the usual type representing the band heads is

$$\nu_h(v', v'') = 30546.1 + (929.3v' - 2.75v'^2) - (1035.2v'' - 9.58v''^2)$$

and one representing the zero lines is

$$\nu_0(v', v'') = 30518.10 + (934.8v' - 2.6v'^2) - (1041.9v'' - 9.35v''^2)$$

Using these formulae and assuming B_2 as the carrier of the band system, a calculation of the isotope shifts $\nu(B^{11}B^{10}) - \nu(B^{11}B^{11})$ according to well-known relations yields the values given in the third column of Table II. The corresponding observed values are given in the second column. While for the bands 2-1, 3-2, 4-3, for which only the heads have been measured, the agreement is within the accuracy of the measurements, there is a definite small discrepancy for the 0-0 and 1-0 bands, whose zero lines have been accurately determined. It is not possible to obtain a better agreement by assuming another emitter of the band system since fitting the one shift throws the other off still more. We are therefore led to the conclusion that a vibrational perturbation occurs for the $v' = 0$ and 1 levels of $B^{11}B^{10}$ which does not occur or not to such an extent for $B^{11}B^{11}$. It seems that such an occurrence is possible.

TABLE II
COMPARISON OF OBSERVED AND CALCULATED ISOTOPE SHIFTS

| Band | $\nu(B^{11}B^{10}) - \nu(B^{11}B^{11})$ | | Difference, Obs. - calc. |
|-------|---|------------|-----------------------------|
| | Observed | Calculated | |
| 0 - 0 | - 0.67* | - 1.32* | +0.65 |
| 1 - 0 | +22.00* | +21.46* | +0.54 |
| 2 - 1 | +20.6** | +20.3** | +0.3 |
| 3 - 2 | +19.1** | +18.4** | +0.7 |
| 4 - 3 | +17.9** | +17.5** | +0.4 |

* Refers to band origins.

** Refers to band heads.

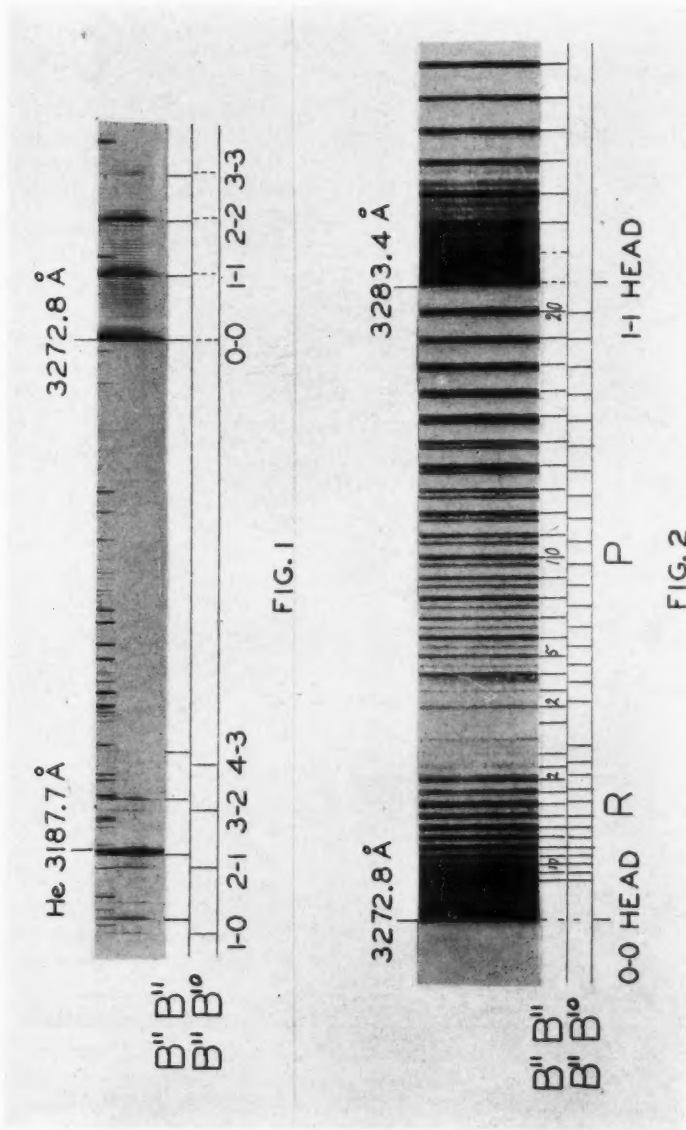
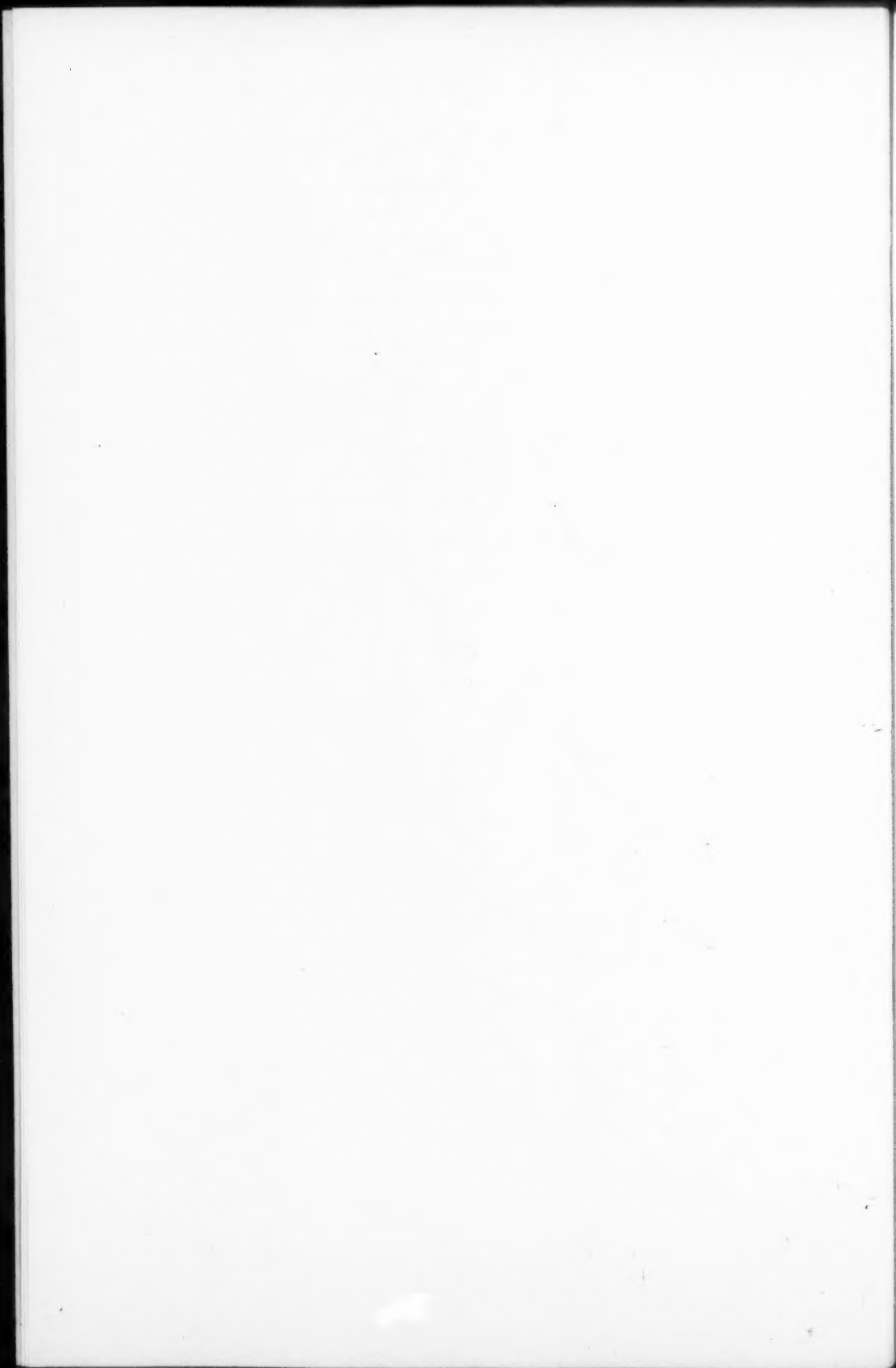


FIG. 1 Band system of the B_2 molecule. FIG. 2 Fine structure of the $0-0$ band of the $\Sigma_u^- - \Sigma_g^-$ bands of B_2 .



Apart from the intensity alternation observed in the fine structure (see below), the assumption that B_2 is the emitter of the band system is also confirmed by the observation that the intensity ratio of the isotopic to the corresponding main bands is much larger than for the band systems of BN or BO, in agreement with expectation for B_2 for which it should be about 1 : 2 instead of 1 : 4. Finally, a very weak band head is found at 31518.6 cm^{-1} which fits well the expected position of the $B^{10}B^{10}$ 1-0 band, the only one lying in a sufficiently favourable position to be observed.

Rotational Analysis

The fine structure of the bands is of the simplest type: they have only one P and one R branch each. This is shown in Fig. 2, which gives an enlarged reproduction of the 0-0 band. Since for this band and the 1-0 and 1-1 bands both branches are resolved, the determination of the numbering can be made according to well-known methods [see, for example, Herzberg (3)]. Table III gives the wave numbers of the lines of the 0-0, 1-0, and 1-1 bands of $B^{11}B^{11}$, and Table IV, those of the 0-0 and 1-0 bands of $B^{11}B^{10}$ with the final numbering obtained. Table V gives the combination differences $\Delta_2 F'(J) = R(J) - P(J)$ and $\Delta_2 F''(J) = R(J-1) - P(J+1)$ for the $B^{11}B^{11}$ bands. The excellent agreement of the $\Delta_2 F'(J)$ for

TABLE III
WAVE NUMBERS OF THE LINES IN THE $B^{11}B^{11}$ BANDS

| J | 0-0 Band | | 1-0 Band | | 1-1 Band | |
|-----|------------|----------|----------|----------|----------|----------|
| | $P(J)$ | $R(J)$ | $P(J)$ | $R(J)$ | $P(J)$ | $R(J)$ |
| 0 | | 30520.37 | | | | |
| 1 | 30515.72 | 22.57 | | | | 30422.22 |
| 2 | 13.22 | 24.64 | | | | 24.31 |
| 3 | 10.55 | 26.60 | | | | 26.27 |
| 4 | 07.87 | 28.57 | | | | |
| 5 | 05.06 | 30.41 | | 31462.18 | | 30.07 |
| 6 | 02.19 | 32.15 | 31434.03 | 63.64 | | 31.83 |
| 7 | 30499.11 | 33.74 | 31430.80 | 65.15 | 30399.14 | |
| 8 | 96.01 | 35.30 | | 66.43 | 96.08 | 34.97 |
| 9 | 92.86 | 36.77 | 24.17 | 67.56 | 92.96 | 36.44 |
| 10 | 89.54 | 38.05 | 20.74 | 68.66 | 89.77 | |
| 11 | 86.14 | 39.24 | 17.10 | 69.62 | 86.51 | 39.02 |
| 12 | 82.63 | 40.36 | 13.36 | 70.42 | 83.05 | 40.23 |
| 13 | 79.03 | 41.31 | 09.47 | 71.13 | 79.55 | 41.34 |
| 14 | 75.36 | 42.23 | 05.49 | 71.73 | 76.04 | |
| 15 | 71.56 | | 01.37 | | 72.32 | |
| 16 | 67.65 | | 31397.18 | | 68.59 | |
| 17 | 63.66 | | | | 64.72 | |
| 18 | 59.35 | | | | | |
| 19 | 55.40 | | | | | |
| 20 | 51.22 | | | | | |
| 21 | Overlapped | | | | | |
| 22 | 42.22 | | | | | |
| 23 | 37.62 | | | | | |
| 24 | 33.02 | | | | | |
| 25 | 28.14 | | | | | |

TABLE IV
WAVE NUMBERS OF THE LINES IN THE B¹⁰B¹¹ BANDS

| J | 0-0 Band | 1-0 Band | |
|----|----------|----------|----------|
| | P(J) | P(J) | R(J) |
| 4 | 30506.59 | | |
| 5 | 03.67 | | |
| 6 | 00.57 | 31455.19 | |
| 7 | 30497.41 | 51.85 | 31487.99 |
| 8 | 94.17 | 48.49 | 89.23 |
| 9 | 90.80 | | 90.45 |
| 10 | 87.37 | | 91.55 |
| 11 | 83.80 | 37.37 | 92.60 |
| 12 | 80.10 | | 93.40 |
| 13 | 76.32 | | |
| 14 | 72.46 | | |
| 15 | 68.52 | | |
| 16 | 64.44 | | |
| 17 | 60.20 | | |
| 18 | 55.93 | | |

TABLE V
COMBINATION DIFFERENCES $\Delta_2 F(J)$ FOR THE B₂¹¹ BANDS

| J | $\Delta_2 F''(J) = R(J-1) - P(J+1)$ (lower state) | | | $\Delta_2 F'(J) = R(J) - P(J)$ (upper state) | | |
|----|--|----------|----------|---|----------|----------|
| | v'' = 0 | | v'' = 1 | v' = 0 | | v' = 1 |
| | 0-0 Band | 1-0 Band | 1-1 Band | 0-0 Band | 1-0 Band | 1-1 Band |
| 1 | 7.15 | | | 6.85 | | |
| 2 | 12.02 | | | 11.42 | | |
| 3 | 16.77 | | | 16.05 | | |
| 4 | 21.54 | | | 20.70 | | |
| 5 | 26.38 | | | 25.35 | | |
| 6 | 31.30 | 31.38 | | 29.96 | 29.61 | |
| 7 | 36.14 | 36.08 | 35.75 | 34.63 | 34.35 | |
| 8 | 40.88 | 40.98 | | 39.29 | 38.87 | 38.89 |
| 9 | 45.76 | 45.69 | 45.20 | 43.91 | 43.39 | 43.48 |
| 10 | 50.63 | 50.46 | 49.93 | 48.51 | 47.92 | |
| 11 | 55.42 | 55.30 | | 53.10 | 52.52 | 52.51 |
| 12 | 60.21 | 60.15 | 59.47 | 57.73 | 57.06 | 57.18 |
| 13 | 65.00 | 64.93 | 64.19 | 62.28 | 61.66 | 61.79 |
| 14 | 69.75 | 69.76 | 69.02 | 66.87 | 66.24 | |
| 15 | 74.58 | 74.55 | | | | |

the 1-0 and 1-1 bands and of the $\Delta_2 F''(J)$ for the 0-0 and 1-0 bands proves unambiguously the correctness of the numbering used. From the combination differences the rotational constants B_v were obtained in the usual manner using for the rotational constants D the values calculated from $D = \frac{4B^3}{\omega^2}$ with preliminary B 's. The B_v and D values are given in Table VI. The values of B_v and α following from them as well as the resulting

values of the moments of inertia and the internuclear distances, are summarized in Table VII together with the vibrational constants.

TABLE VI
ROTATIONAL CONSTANTS

| v | Upper state, $^3\Sigma_u^-$ | | Lower state, $^3\Sigma_g^-$ | |
|-----|-----------------------------|---------------------------|-----------------------------|---------------------------|
| | B_v' , cm. ⁻¹ | D' , cm. ⁻¹ | B_v'' , cm. ⁻¹ | D'' , cm. ⁻¹ |
| 0 | 1.155 | (7.0 · 10 ⁻⁶) | 1.205 | (6.5 · 10 ⁻⁶) |
| 1 | 1.144 | | 1.191 | |

TABLE VII
MOLECULAR CONSTANTS OF B₂¹¹

| | Upper state, $^3\Sigma_u^-$ | Lower state, $^3\Sigma_g^-$ |
|---|-----------------------------|-----------------------------|
| B_v , cm. ⁻¹ | 1.160 | 1.212 |
| α , cm. ⁻¹ | 0.011 | 0.014 |
| I_v , gm.-cm. ² | 24.13 · 10 ⁻⁴⁰ | 23.10 · 10 ⁻⁴⁰ |
| r_v , cm. | 1.625 · 10 ⁻⁸ | 1.590 · 10 ⁻⁸ |
| r_0 , cm. | 1.628 · 10 ⁻⁸ | 1.594 · 10 ⁻⁸ |
| ω_v , cm. ⁻¹ | 937.4 | 1051.3 |
| ω_0 , cm. ⁻¹ | 934.8 | 1041.9 |
| $\omega_e x_e = \omega_0 x_0$, cm. ⁻¹ | 2.6 | 9.4 |
| A_0 (excitation energy), cm. ⁻¹ | 30518.10 | 0 |

Intensity Alternation, Nuclear Spin

The final proof that the emitter of the new band system is the B₂ molecule is supplied by the clear intensity alternation occurring in those bands of the more abundant isotope (B¹¹B¹¹) whose fine structure is well resolved. It can be seen in the spectrogram of the 0-0 band reproduced in Fig. 2. As it should be, in the series formed by the *P* and *R* branch the strong lines of the *P* branch form the continuation of the weak lines of the *R* branch. The lines with even *J* are the strong ones in each branch. It is very significant and agrees with expectation that the lines of the B¹¹B¹⁰ bands do not show any intensity alternation, as is also clearly shown by Fig. 2.

The intensity ratio of the strong to the weak lines of a homonuclear molecule is given by $\frac{I+1}{I}$, where *I* is the nuclear spin. Since B¹¹ has an odd number of particles of spin $\frac{1}{2}$ (neutrons and protons), its spin would be expected to be half-integral. The intensity alternation for *I* = 1/2, *I* = 3/2, and *I* = 5/2 is 3 : 1, 1.67 : 1, and 1.40 : 1 respectively. A mere inspection of Fig. 2 shows that the first value is out of the question. But the distinctness of the alternation seems to point to the second value, as was suggested in the pre-

liminary account of this work (2). However, subsequent, more accurate intensity measurements with the aid of intensity marks have led to the intensity ratio of alternate lines 1.42 : 1, which agrees within the accuracy of the measurements (about 10%) with the theoretical value corresponding to $I = 5/2$, but not $I = 3/2$. The fact that two independent measurements with two different microphotometers gave concordant results (1.43 : 1 and 1.39 : 1) seems to make this value rather definite. On the other hand, according to the Hartree model a value of $I = 3/2$ [see Rose and Bethe (6)], and according to the α -particle model a value of $I = 1/2$ or $3/2$ [see Sachs (7)] has been predicted for the B^{11} nucleus. According to both theories the ground state is expected to be a 2P state. The above evidence seems to show that the next higher predicted level 2D actually forms the ground state of the B^{11} nucleus with the $^2D_{5/2}$ component lower than $^2D_{3/2}$.

It should be mentioned that, on the basis of an abundance ratio of 4 : 1 for the two boron isotopes and of a B^{11} spin of $5/2$, the intensity ratio of the weak B_2^{11} lines to the $B^{11}B^{10}$ lines of the 0-0 band should be 1 : 1.7 whereas they appear to have almost the same intensity (see Fig. 2) as is also confirmed by the intensity measurements. This discrepancy is apparently related to a similar discrepancy found by Elliott (2a) for the intensity ratio of the $B^{11}O$ and $B^{10}O$ bands [see also Jenkins and Ornstein (4a)]. It may also be connected with the fact that there is a perturbation in the upper state (see above). However this discrepancy can hardly be ascribed to an error in the determination of the intensity alternation in the B_2^{11} band since only an intensity alternation 3 : 1 which is clearly impossible (see Fig. 2) would lead to a 1 : 1 ratio of the intensity of the weak lines of B_2^{11} to the lines of $B^{11}B^{10}$.

Because of the importance of the question, experiments are under way in this laboratory to check the I value of B^{11} given above by investigating another band system of B_2 if such can be found. Also it is hoped that it will be possible to obtain a $B^{10}B^{10}$ band with sufficient intensity to permit measurement of the intensity alternation in it and determination of the spin of B^{10} .

With the above value of I of B^{11} and using Millman, Kusch, and Rabi's (5) nuclear g factor, the magnetic moment of the B^{11} nucleus comes out to be 4.47 nuclear magnetons.

Electronic Structure, Comparison with Other Molecules

The fact that each band has a P and an R branch only shows that the band system represents a $\Sigma - \Sigma$ transition. Nothing definite can be said about the multiplicity since only lines of fairly low J values have been measured and since for Σ states the multiplet splitting is usually noticeable only for large J values, particularly for light molecules. If Fermi statistics is assumed for the B^{11} nuclei, the fact that the even lines are the strong ones shows that the transition is either $\Sigma_u^- - \Sigma_g^-$ or $\Sigma_g^+ - \Sigma_u^+$.

The electron configuration of the ground state of B_2 is, according to the Hund-Mulliken scheme,

$$(K)(K)(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p)^2,$$

which gives rise to the states $^3\Sigma_g^-$, $^1\Delta_g$ and $^1\Sigma_g^+$. In the molecules C_2 and N_2^+ , and in the heteronuclear molecules having the same number of electrons as either, a transition from an excited state, in which an electron is brought from the $\sigma_u 2s$ to the $\sigma_g 2p$ shell, to the ground state gives rise to the strongest band system. In B_2 such an excited electron configuration

$$(K)(K)(\sigma_g 2s)^2(\sigma_u 2s)(\pi_u 2p)^2(\sigma_g 2p)$$

gives rise to the states $^3\Sigma_u^-$, $^1\Delta_u$, $^1\Sigma_u^+$, $^1\Sigma_u^-$, $^5\Sigma_u^-$, $^3\Delta_u$, $^3\Sigma_u^+$. It is significant that one and only one transition from this group of states to the group resulting from the ground electron configuration fits the observed structure, namely the transition $^3\Sigma_u^- - ^3\Sigma_g^-$. It is therefore very likely that the observed transition is this transition between the two electron configurations given, particularly since otherwise the lower state of the bands would have to be a very highly excited state of the B_2 molecule. Thus we conclude that the lower state of the bands is the ground state of the B_2 molecule. It is of course desirable to show that a triplet splitting occurs for the lines with larger J values but thus far we have not been able to do so for lack of intensity.

It is significant that the assumption of Fermi statistics for the B^{11} nuclei leads to reasonable results, since it is the statistics one would expect for this nucleus on the basis of modern nuclear theory. The more critical statistics of the B^{10} nuclei (see Introduction) will be obtainable from the $B^{10}B^{10}$ bands without any assumption about the electronic structure once Fermi statistics is assumed for B^{11} . Here again we have not yet solved the problem of getting a sufficient intensity of the B_2 bands.

Under the likely assumption (see above) that the lower state of the B_2 bands is the ground state of the molecule, it is interesting to compare the the r_e'' and ω_e'' values with those for the ground states of the other elementary molecules of the second period of the periodic system. This is done in Table VIII. It is seen that the values for B_2 fit in very well. The minimum of r_e and maximum of ω_e in this series of molecules occurs of course for nitrogen with its triple bond.

It is also interesting to compare the internuclear distance r_e'' and the force constant k_e'' (obtained from ω_e'') in B_2 with the B—B distance and force

TABLE VIII

COMPARISON OF INTERNUCLEAR DISTANCES AND VIBRATIONAL FREQUENCIES OF ELEMENTARY MOLECULES OF THE SECOND PERIOD OF THE PERIODIC SYSTEM IN THEIR GROUND STATES

| | He ₂ | Li ₂ [†] | Be ₂ | B ₂ ¹¹ | C ₂ | N ₂ | O ₂ | F ₂ | Ne ₂ |
|-------------------------------|-----------------|------------------------------|-----------------|------------------------------|----------------|----------------|----------------|----------------|-----------------|
| $r_e'', 10^{-8}$ cm. | Very large | 2.672 | ? | 1.590 | 1.312 | 1.095 | 1.208 | 1.45 | Very large |
| $\omega_e'', \text{cm.}^{-1}$ | 0 | 351.35 | ? | 1051.3 | 1641.7 | 2359.6 | 1580.4 | ? | 0 |

constant in B_2H_6 , on the one hand, and with the C—C distance and C—C force constant in C_2 and C_2H_6 , on the other, as in Table IX. It is seen that the internuclear distance in the free radicals is smaller than in the polyatomic

TABLE IX
INTERCOMPARISON OF B—B AND C—C DISTANCES AND FORCE
CONSTANTS IN X_2 AND X_2H_6 ($X = B$ OR C)

| | r_0 , 10^{-8} cm. | $k_0(X-X)$, 10^6 dynes/cm. |
|----------|-----------------------|-------------------------------|
| B_2 | 1.594 | 3.520 |
| B_2H_6 | 1.86* | 3.57* |
| C_2 | 1.316 | 9.392 |
| C_2H_6 | 1.55** | 5.62** |

* See Anderson and Burg (1).

** See Stitt (8).

molecules. This behaviour is opposite to the one found when $r(C-C)$, $r(C-N)$, $r(C-H)$ of C_2 , CN, CH are compared with the values in C_2H_2 , HCN, and CH_4 [see Herzberg, Patat, and Verleger (4)]. The reason is obviously that in the present case the valency of the bond in the polyatomic molecule is lower than in the diatomic molecule, whereas in the molecules C_2H_2 , HCN, CH_4 the particular bond has its highest valency. One would expect just the opposite relations to hold for the force constant. While this is actually the case for the C—C, C—N, and C—H bonds, it is not so for the B—B bond, which has about the same force constant in B_2 and B_2H_6 . It should however be noted that the force constants particularly in non-linear molecules cannot be very definitely determined since they depend to some extent on the force system assumed. Still, the difference between the pairs B_2 — B_2H_6 and C_2 — C_2H_6 is rather marked.

Acknowledgments

We are extremely grateful to Dr. H. J. Yearian (Purdue University) and Mr. R. E. Harrington (University of California) for taking the microphotometer curves which led to the determination of the nuclear spin of B^{11} . We are greatly indebted to the American Philosophical Society for a grant from the Penrose Fund through which the grating spectrograph was provided.

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IMPROVED POLE PIECE CONSTRUCTION OF THE OBJECTIVE LENS OF A MAGNETIC ELECTRON MICROSCOPE¹

BY ALBERT PREBUS²

Abstract

The paper is a description of a new form of pole piece devised for the electron microscope developed at the University of Toronto.

In a previous publication (1) the construction of a magnetic electron microscope of high resolving power was described. In order to reduce the magnitude of the image errors which result from imperfect alignment of the pole pieces of the objective lens, a novel method has been adopted for constructing the pole-piece unit, this unit consisting of the two pole pieces and the spacer between them. Figs. 1 and 2, which are cross-sectional diagrams of the previously described and the new type of pole-piece unit, facilitate the description of the improved method of construction and the advantages gained thereby. In both figures, *A* represents the upper iron disc of the objective lens; *B* the inner iron sleeve; and *C* the coil.

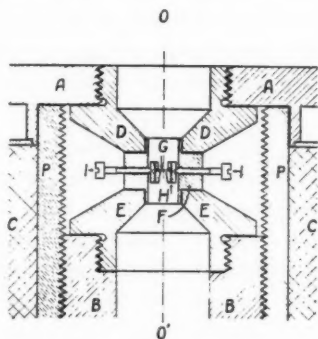


FIG. 1

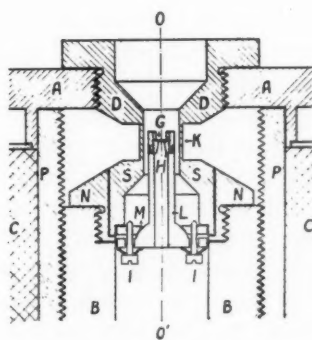


FIG. 2

In Fig. 1, *D* represents the upper pole piece, which is threaded into the disc *A*; *E* the lower pole piece, which is threaded into the sleeve *B*; and *F* the brass spacer, the purpose of which is to fix the length of the gap between the pole pieces and to align their axes of symmetry. A platinum diaphragm *G* (aperture diameter, 0.025 mm.), is fastened in a capsule *H* midway in the gap between the pole pieces. By means of four set screws *I*, the centre of the diaphragm aperture can be fixed in the axis of symmetry *OO'*. Although great

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care was exercised in the machining of the pole pieces and the spacer to ensure axial symmetry of each of these parts, it was found that the axial symmetry of the entire unit, and consequently the axial symmetry of the magnetic field in the gap, was imperfect. Further, variations of this asymmetry with the intensity of the magnetic field indicated that the contact of the pole pieces with the remainder of the iron sheath was unsymmetrical. The distortions in the magnetic field caused by these mechanical imperfections resulted in serious image defects.

Fig. 2 illustrates the new method of pole-piece construction, which has reduced these difficulties considerably. The feature of this pole-piece assembly which has made possible the attainment of a higher degree of precision in symmetry, is the use of a thin walled tube of iron in place of the usual spacer made of non-ferromagnetic material. A simple calculation indicates that a cylindrical tube with a wall thickness of approximately 0.5 mm., when placed in the gap between the pole pieces, will become saturated at a value of the field intensity that is small compared with the value that exists at any point in the gap when the lens is in operation. An iron tube of this description possesses adequate mechanical strength to maintain the alignment of the pole pieces, and it has been found that its magnetic properties are not injurious to the optical properties of the field. It is apparent that the use of such a spacer with sufficient wall thickness to cause appreciable changes in the field strength in the gap provides an added variable that may be of value in modifying the third order lens errors.

With an iron spacer, it is possible to construct the upper pole piece *D*, the spacer *K* itself, and the upper part *S* of the lower pole piece from a single piece of material. Further, all the surfaces of these three parts, with the exception of the enlarged cylindrical opening in the upper pole piece, can be machined in a single operation without removing the material from the chuck of the lathe. It is then possible, by mounting this part of the unit on a mandrel, to grind with precision all the external surfaces in one operation. This procedure ensures the highest precision in the axial symmetry of the most important surfaces of the pole-piece unit.

In the case of the unit described herein, the base *N* of the lower pole piece is separable from the remainder. It is first machined roughly, then fitted carefully to the upper part *S* of the lower pole piece while this part of the unit is being machined. This assembly is then finished as a single unit. To minimize the effects of unsymmetrical contact of the pole pieces with the disc *A* and sleeve *B*, these surfaces of contact are ground together. The diaphragm capsule *H*, fastened at the upper end of the tube *L*, is fixed in position by means of the ball and socket joint *M* and four set screws *I*.

In a second microscope at present under construction, the design of the lenses has been modified further with the object of improving the mechanical

contact of the pole pieces with the upper disc *A* and the inner sleeve *B*. The lower end of the sleeve *B* is permanently fixed in the lower iron disc of the lens (a shrink fit). The internal surfaces of the upper end of this sleeve and of the upper disc *A* are machined and ground so that they form two sections of a cone, and the two pole pieces are ground to form the corresponding male sections of the conical union.

Reference

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ERRATUM

Page 93, second line under the heading " *α -Phenyl- β -aminobutyric Acid*",
for "7.0" read "710".

*(Please cut on dotted line and attach the upper gummed strip to page 93 of Section B of the
March, 1940 (Volume 18, No. 3), issue of the Canadian Journal of Research.)*

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NOVEMBER, 1940

NUMBER 11

THE DETERMINATION OF THE METALS OF THE PLATINUM GROUP IN NICKEL ORES AND CONCENTRATES¹

By F. E. LATHE²

Abstract

Most published methods for the determination of platinum and associated metals are not of general application to ores and concentrates, and their accuracy as applied to unknown material is in many cases seriously open to question. The methods here described are chiefly based upon experience with the products of the Sudbury area, but are believed to be applicable without substantial modification to all sulphide ores of nickel and to smelter and refinery products derived therefrom. Methods of concentrating the platinum metals are described, an outline is given of an approximate method of determination based on sulphuric acid parting, and details of a more reliable method in which nitric acid is the parting medium are set out. The results obtained are compared with those of Beamish and associates on similar material.

Introduction

So far as the writer is aware, no simple and at the same time reliable methods for the determination of metals of the platinum group in ores and concentrates have yet been published. If such methods exist, those who might be expected to know most about them are apparently disinclined to share their knowledge with others. There is in the literature much that is uncertain, contradictory, or inapplicable to any particular case.

Gilchrist and Wichers (12) of the U.S. Bureau of Standards have published separations which appear to be almost as simple and accurate as those for the base metals, but their results were obtained in the analysis of solutions in which all the platinum metals were present in the form of chlorides, a condition rarely if ever encountered in practice. Beamish and associates (1-10) of the University of Toronto have published the results of very extensive experimental work with the platinum group metals; their observations are of interest chiefly to the specialist. These authors did not find the methods of Gilchrist and Wichers entirely satisfactory. Useful contributions have been made by Davis (11) and Griffith (13), who have given details for the determination of platinum and palladium. The J. Bishop and Company Platinum Works has published an outline of separations in which the recommendations of other authorities are combined with that company's own methods.

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Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 943.

² Chemist.

The methods described below are neither simple nor novel, but they are offered because they have given satisfactory results in the hands of the writer and various others to whom they have been made privately available from time to time. They are based upon experience with the Granby Consolidated Mining, Smelting and Power Company and the British America Nickel Corporation, and in particular with the latter, where the writer for some years investigated methods of analysis and concentration of the platinum group metals. The B.A.N.C. methods were in turn based upon those used at the nickel refinery at Kristiansand, Norway, but the latter were found to require substantial modification when applied to the ores and products of the Sudbury district.

Nature of the Problem

The problem is essentially threefold. First, while the assayer engaged in the determination of gold and silver in ores and metallurgical products seldom encounters metals of the platinum group, he wishes to know whether, if they occur in any particular case, their presence will be detected in the ordinary course of analysis or if they will merely contaminate the gold and silver and be reported as such.

Second, when it is known or suspected that the platinum group metals are present, a partial or complete determination is required. The nature or amount of the sample available frequently does not justify an attempt to make an accurate determination of all the platinum metals; it is therefore of interest to know what information regarding the nature and quantity of platinum metals can be obtained with a minimum of effort, and in what respects the assays are likely to be in error.

Third, in the case of shipments of nickel ore, matte, concentrates, or refinery slimes, the amount of money involved is sufficient to justify the observance of elaborate precautions in the separation and determination of gold, silver, and as many metals of the platinum group as are present in appreciable quantity and will be paid for by the purchaser. In an extreme case, to be described below, the amount of platinum metals present was a deciding factor in the sorting of ore prior to smelting.

Evidence is not wanting to show that even assayers of wide experience may make serious errors in determining the metals of the platinum group. For example, a sample of the matte first produced by the B.A.N.C. (concentrated in a ratio of about 25:1 from the ore) was sent to one of the most reliable assayers in the United States; a certificate was received showing the approximate platinum metal content of the matte, together with an accompanying letter, in which it was explained that on such material the assayer could do little more than "express an opinion" based on the evidence available. Again, a sample was sent to a prominent refiner of platinum metals, who reported about 50% more platinum than palladium,—whereas the latter was actually present in the larger proportion. In a third case, shipments were made of B.A.N.C. refinery slimes containing 5 to 8% of the platinum group metals, and a maximum difference of about 1% (25 to 30% of the weight

of each metal present) was found between the assays of shipper and refiner for both platinum and palladium. In this instance it was eventually recognized that the shipper's methods were the more reliable.

Properties of Platinum and Associated Metals

It is remarkable that wherever (so far as the writer is aware) nickel has been found in the form of sulphide there are associated with it iron, cobalt, copper, silver, gold, and the whole group of platinum metals. The relation of these metals to one another is shown in Table I.

TABLE I
PERIODIC GROUPING OF PLATINUM AND ASSOCIATED
METALS, WITH ATOMIC NUMBERS

| Group VIII | | | Group I |
|------------|----------|----------|----------|
| Fe 26 | Co 27 | Ni 28 | Cu 29 |
| Ru 44 | Rh 45 | Pd 46 | Ag 47 |
| Os 76 | Ir 77 | Pt 78 | Au 79 |

The chemist who assays for the platinum metals will do well to bear this grouping in mind, for it is closely tied up with the properties and separation of the metals. Ruthenium and osmium are the two platinum metals of highest melting-point, but their tetroxides (the only ones known*) are readily volatile at slightly elevated temperatures. The order of increasing melting point of the metals—palladium, platinum, rhodium, iridium, ruthenium, and osmium—is approximately that of increasing resistance to acid attack. The last four of these metals (in the proportions in which they occur in nickel sulphide ores) are almost completely insoluble in both nitric acid and aqua regia, thereby providing a convenient method of separation from platinum and palladium, both of which dissolve fairly readily under the conditions to be described. In fact, palladium, the least noble of the whole group, is soluble in hot nitric acid, even when in dense form, such as foil. Nickel and palladium are precipitated quantitatively by dimethylglyoxime, and platinum is also precipitated under certain conditions. Copper, silver, and gold are readily attacked by soluble cyanides, but are highly resistant to fused alkali.

The Detection of Platinum Metals in Assaying for Gold

The platinum metals will on rare occasion be present in sufficient quantity to affect the appearance of the silver bead, but reliance should not be placed upon this method of detection. In small proportion they give the silver

* Prof. Beamish informs the writer that he has obtained indications of the formation of iridium tetroxide.

bead a slightly dull appearance. If the colour of the gold bead obtained in parting with nitric acid is abnormal, the possibility of the presence of platinum metals should always be investigated.

Two other indications obtained in parting are of greater significance. If the proportion of platinum metals to gold be even a few parts per hundred, their presence will ordinarily be indicated in two ways,—by “flouring” of the gold, and by the reddish-brown colour of the solution. If neither of these conditions be observed it may be safely concluded that little, if any, platinum or palladium, the commonest metals of the platinum group, is present.

“Flouring” of the gold is the breaking up of the bead to such a state of fineness that it becomes difficult, if not impossible, to wash it safely by the usual method of decantation. The reddish-brown coloration is caused by solution of platinum and palladium in nitric acid. Palladium is particularly effective in colouring the solution.

Approximate Determination by Sulphuric Acid Method

When the presence of the platinum metals is thus detected it is usually necessary to determine at least the approximate total amount of metals of this group present. For this purpose it is desirable to run a separate assay, adding to the crucible or scorifier used at least 20 times as much silver as the total amount of the gold and platinum metals believed to be present,—a greater proportion does no harm. The silver bead is then parted with concentrated sulphuric acid and the residue is weighed as combined gold and platinum metals. If palladium be present with the platinum, as is usually the case, it will largely go into solution and will make its presence evident by the reddish-brown colour of the liquid. It may be determined by precipitation with dimethylglyoxime, as described below. An outline of this method is given in Fig. 1.

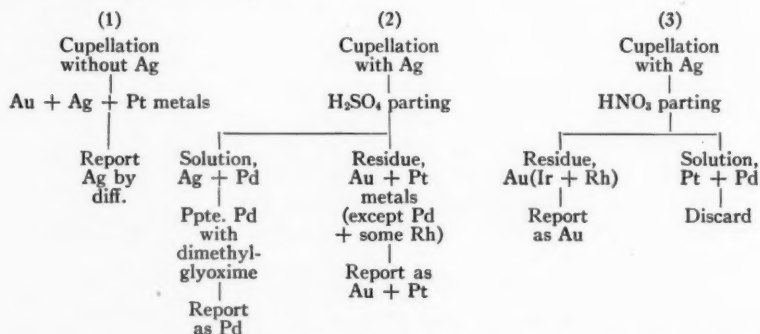


FIG. 1. *Approximate method for the determination of platinum metals, gold, and silver.*

If the quantity of metals of the platinum groups proves to be sufficient to justify further work, a partial separation may be made by treatment of the

residue with aqua regia, which dissolves gold, platinum, and palladium, but for a more accurate determination reference is made to the methods to be described below.

Dry assays, such as that described by Seath and Beamish (10), do not give satisfactory results on nickel sulphide ores.

Preliminary Concentration of the Platinum Metals

The methods of concentration to be adopted will depend chiefly upon the grade of material being assayed. It is desirable for an accurate separation and determination of the platinum metals to have a total quantity of 5 to 10 mg. of these metals with which to work, and this usually requires the use of a large sample. Even in the case of the ores of the Sudbury area, which now leads the world in the production of platinum metals, the proportion present is usually so small that a weight of ore in the order of 50 to 100 assay tons should preferably be used. This may be concentrated by fusing with excess litharge flux and combining the lead buttons, followed by repeated scorification to eliminate nickel and copper, or the whole quantity may be fused to a matte in a single operation, as in a large crucible in a gas-fired furnace.

In the determination of platinum metals in rock-house waste, referred to above, the writer used triplicate samples of 25 kg. each and reduced these to matte by smelting with suitable fluxes, thereby effecting a concentration of 10 : 1. A further concentration of 5 : 1 was made by treating the matte with hydrochloric acid (1 : 1) to remove iron and nickel sulphides, following which the residues were fused in several portions with lead oxide in crucibles and repeatedly scorified with test lead to remove copper. The charges were cooled in the crucibles and the latter were broken to release the lead buttons,—a desirable precaution in order to avoid possible loss of iridium, rhodium, and osmium, which do not alloy with lead. This treatment substantially eliminates nickel, which, according to Seath and Beamish (10), prevents complete collection of platinum metals with lead. The method of concentration is shown in Fig. 2.

If, on the other hand, a very rich material is being assayed, such as concentrated refinery slimes, a sample as small as 100 to 200 mg. may be used. This is scorified with test lead, or, if a determination of ruthenium and osmium is not required, it may be wrapped in lead foil and cupelled directly with 20 gm. of test lead and the silver necessary for parting. A quantity of silver 20 times the total weight of gold and platinum metals present is recommended.

Determinations of ruthenium and osmium are not often required, but if the loss of these metals (as volatile oxides) must be prevented the final lead buttons resulting from any method of concentration should not be cupelled below a weight of 3 to 5 gm. The final buttons may be dissolved directly in nitric acid (1 : 10). This procedure is inconvenient, and it is customary to eliminate the lead by cupellation, using a temperature somewhat higher

than normal. Most of the osmium is likely to be lost in this operation, but if the material being assayed is a converter matte the osmium may indeed have been lost previously during the converter blow. Experimental evidence on this point is lacking.

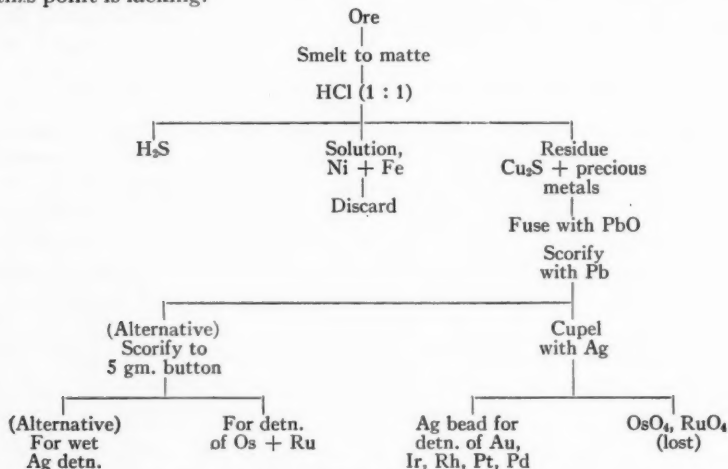


FIG. 2. Concentration of sulphide ore or matte

The cupel should preferably be of a material completely acid soluble, and the silver bead should be removed from it with care in order to avoid the loss of iridium and rhodium, which may be loosely adherent. Possible loss by spitting should be avoided by covering the cupel with an empty hot cupel. The presence of platinum metals greatly increases the tendency to spit.

Proofs

For accurate work the necessity of using proofs can scarcely be overstressed. A separation that is entirely satisfactory for two metals present in certain proportions may become very incomplete if the proportions are substantially different or an additional metal of the platinum group is present. This fact no doubt accounts for many of the discrepancies found in the literature. The use of proofs containing in approximately the right proportions all the platinum metals present is therefore always essential if accurate determinations are required. On unknown material this will of course involve a preliminary assay. In important work the writer has sometimes used as many as three proofs, these containing silver, gold, and the platinum metals in slightly different proportions.

Ruthenium and Osmium

The separation of ruthenium and osmium should begin with the lead button, which, as Russell, Beamish and Seath (6) have shown, cannot safely be cupelled below 3 gm. in weight if as much as 5 mg. of osmium be present. With greater quantities of osmium the button should be left still larger.

Ruthenium and osmium are separated from the other platinum metals by oxidation and distillation. In the presence of appreciable quantities of iridium and rhodium, which usually accompany ruthenium and osmium, the lead button may be dissolved by gently warming with nitric acid (1 : 10), whereupon these metals will be found in the residue and may be filtered off and fused with sodium hydroxide and sodium peroxide in a silver or nickel crucible at a dull red heat. In the absence of iridium and rhodium, or in case of doubt, both the lead solution and the residue should be examined for ruthenium and osmium. Two methods of distillation are available.

According to the method recommended by J. Bishop and Company the melt is dissolved in hot water, the osmium and ruthenium are distilled together in a current of chlorine and are collected in a train of Wouff bottles containing, successively, water, sodium bisulphate, and sodium hydroxide. The distillates are combined and acidified with hydrochloric acid and the metals are reduced with zinc and filtered off. The osmium is dissolved with hydrogen peroxide, leaving a residue of ruthenium, and the osmium is finally precipitated with hydrogen sulphide.

Gilchrist and Wichers (12) separate osmium from ruthenium by distilling the former from a boiling nitric acid solution, of moderate concentration (1 : 1), through which a stream of air is passed. The osmium is collected in hydrochloric acid solution (1 : 1) saturated with sulphur dioxide, and after the destruction of sulphite compounds is precipitated as dioxide from hydrochloric acid solution by means of sodium bicarbonate. Elaborate precautions are necessary to prevent the loss of osmium. The solution from which the osmium was distilled is then evaporated with hydrochloric acid to destroy the nitric acid, sodium bromate is added, the ruthenium is distilled, and it is then collected and precipitated as was the osmium.

The writer has had insufficient experience with ruthenium and osmium to permit a definite recommendation as to the method to be adopted. The chlorine distillation is that usually followed. Gilchrist and Wichers (12) state that the chlorine distillation may give a low result for ruthenium, since some may be precipitated with iridium hydroxide when the solution becomes nearly neutral. They, however, introduce the iridium as chloride, whereas in the procedure described above it remains in the insoluble residue.

Nitric Acid Separation

No known acid, under the conditions usually encountered, will completely dissolve any of the platinum metals from the silver bead and leave the others wholly in the residue. The writer has had the best success with nitric acid, but his experience is in accord with that of Seath and Beamish (8) that two or three treatments are ordinarily required to dissolve all the platinum. An outline of the separation is given in Fig. 3.

The silver bead is transferred without cleaning to a beaker and is warmed with 10 ml. of nitric acid (1 : 1) until action ceases; 6 ml. of sulphuric acid (1 : 1) is added and the liquid is evaporated to fumes. Unnecessary heating

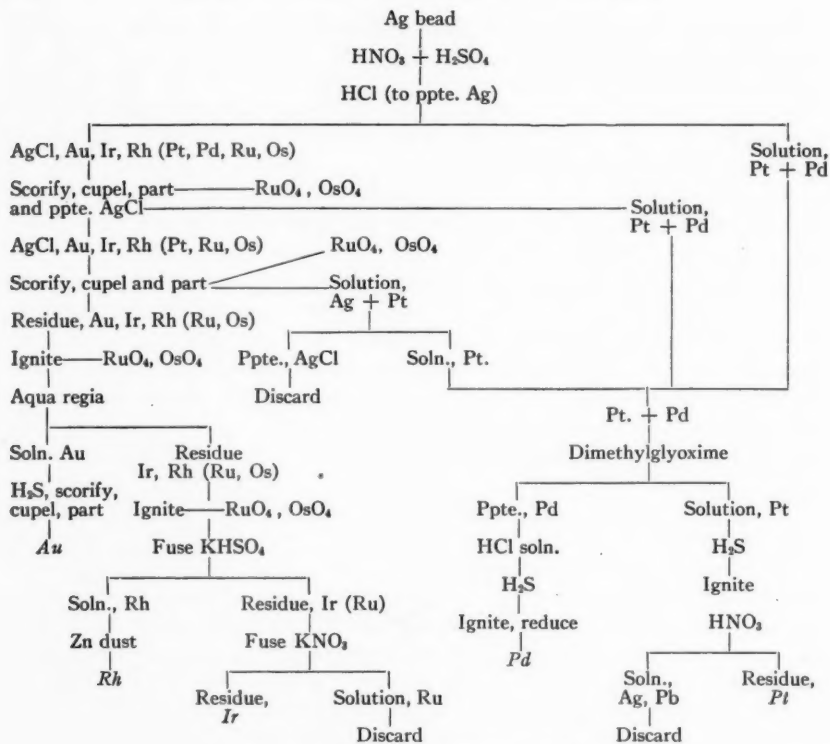


FIG. 3. Separation of platinum metals.

is objectionable, as some rhodium may go into solution. Silver is precipitated with a slight excess of hydrochloric acid in the diluted solution still containing the residue of platinum metals. It is then filtered, dried, scorified with 25 gm. of test lead, cupelled, and parted again in the same way. A second precipitation of silver and a third cupellation and parting are required for accurate work. On taking up the silver sulphate with water after the final parting, no hydrochloric acid is added, but the liquid is filtered and the residue treated as described below. The first two filtrates may be united, but the third is kept separate and silver is precipitated in it as chloride, filtered off, and discarded. The final filtrate may then be combined with the others, which contain the bulk of the palladium and platinum.

In the above parting, the expulsion of the nitric acid is desirable before precipitation of the silver in order to avoid the formation of aqua regia and the possible solution of some gold. If the precipitation of silver is made as described, before combining the filtrates, the separation of the platinum and palladium from silver is complete; otherwise, some palladium will be carried down with the silver chloride.

Aqua Regia Separation

The residue, which contains gold, iridium, and rhodium (also some ruthenium and osmium, if present and not already separated), is washed with hot strong ammonium acetate solution, to dissolve any lead sulphate present, then with ammonia to remove any possible silver chloride, and finally with hot water. The clean residue is dried, the paper is burned, and heating is continued for a short time at a dull red heat to oxidize and expel osmium, and possibly ruthenium. The residue is warmed for one hour with aqua regia (1 : 5) to dissolve the gold; the insoluble iridium and rhodium are then filtered off and washed.

Gold

The gold solution is evaporated three times nearly to dryness with hydrochloric acid to expel nitric acid. Gold is likely to separate as metal if it becomes quite dry. The solution is taken up with water and gold is precipitated in any convenient way, as by sulphur dioxide, oxalic acid, hydroquinone, or a ferrous salt. The writer prefers to precipitate the gold with hydrogen sulphide and to filter, scorify with lead and silver, cupel, and part with nitric acid. The gold is then coherent and easy to wash by decantation.

Iridium and Rhodium

A quantity of two or three grams of alkali bisulphate is fused in a quartz crucible until spattering ceases, then the residue of iridium and rhodium is added and fusion is continued for 10 min. If, on cooling, the lead is distinctly yellow with dissolved rhodium, the fusion is repeated until the final melt is white. The melt is dissolved in hot dilute hydrochloric acid (1 : 10) and the residue is filtered off and weighed as iridium. If much ruthenium is known to have been present originally, some may still remain. This can be removed by fusion with potassium nitrate in a silver dish, but it will not in any case represent the total amount of ruthenium originally present and may therefore be discarded.

The filtrate is evaporated to dryness and the sulphates are dissolved in 20 ml. of hot water and 1 ml. of concentrated hydrochloric acid. If an appreciable quantity of rhodium be present the solution will be red, and the writer has on occasion been able to determine the amount by comparing the colour with that of the proofs. Zinc dust is added and warming is continued for at least one hour. Any excess of zinc is then dissolved with hydrochloric acid and the rhodium filtered off, ignited at a low temperature, treated with a drop of formic acid to reduce any oxide formed, dried, and weighed as metal.

Palladium and Platinum

The filtrates from the three nitric acid partings are combined and evaporated to strong fumes of sulphuric acid. After dilution, the solution is warmed well to dissolve any palladium sulphate, which goes into solution rather slowly, and is allowed to stand for the separation of lead sulphate. This is filtered

off and washed with dilute sulphuric acid (1 : 20). A drop of hydrochloric acid is added and the solution is allowed to stand for some hours for the separation of any silver that may remain. If a precipitate forms it is filtered off.

The dimethylglyoxime precipitation of palladium is very satisfactory if precautions are taken to avoid the precipitation of platinum. The reagent is not always of high purity and should be recrystallized by cooling a hot saturated alcoholic solution. The solution of palladium and platinum should be brought to the proper degree of acidity, as by neutralizing with ammonia and then adding 3 to 5% of its volume of concentrated hydrochloric acid. Precipitation should be carried out at room temperature by adding 10 ml. or more of a 1% alcoholic solution of dimethylglyoxime, and the lemon-yellow precipitate is filtered off after standing only 10 or 15 min. A relatively open filter paper is satisfactory.

The platinum compound, when formed, is anisotropic, being blue in one direction and bronze in the other. A greenish tint to the palladium precipitate therefore usually indicates the presence of platinum. In such a case the precipitate should be dissolved in hot hydrochloric acid (1 : 1), adjusted to the proper acidity and reprecipitated, but if the above precautions are taken the platinum will remain in solution.

The palladium precipitate, if large, may be weighed as such, or if small may be ignited gently to metal, but since the carbon is difficult to burn off completely and the ignition of this precipitate frequently leads to the loss of a little palladium, it is safest to dissolve it in hot hydrochloric acid (1 : 1), oxidize it with a little nitric, expel these by evaporating with sulphuric and finally precipitate in hot slightly acid solution with hydrogen sulphide. It is well to continue passing the gas until the solution reaches room temperature and then allow it to stand overnight before filtering. When the precipitate has been ignited it should be moistened with a little formic acid* to reduce surface oxide, and dried at about 60° C. in order to avoid reoxidation, which takes place very readily.

To the filtrate from the dimethylglyoxime precipitate there is added 10% of its volume of concentrated hydrochloric acid, since platinum sulphide is more insoluble in such a solution than in weaker acid. The liquid is then heated to boiling and hydrogen sulphide is passed in until the solution is cold. After standing overnight the precipitate is filtered off and ignited at the lowest possible temperature. The metal is then treated with a little nitric acid (1 : 3) to dissolve any lead or silver that may possibly be present, and is filtered, ignited, and weighed as platinum. Some may prefer to scorify the sulphide with test lead and silver, cupel and part with sulphuric acid.

Silver

Owing to the loss of silver in cupellation when appreciable quantities of platinum metals are present, this element cannot be accurately determined

* Professor Beamish considers reduction by formic acid to be incomplete. Proofs will, in part at least, correct for incomplete reduction, or reoxidation.

in the usual way. The lead button containing the silver may be scorified to 3 to 5 gm. and the latter is then dissolved in nitric acid (1 : 4). The insoluble residue is filtered off and the silver is precipitated in the filtrate as chloride. This is freed from palladium by solution in ammonia and reprecipitation and is finally weighed as chloride or cupelled to metal. The latter may, as a check, be parted with nitric acid, but any residue should be negligible in quantity.

Corrections

The corrections necessary, as indicated by the proofs, may be either positive or negative, but will usually be small, except in the case of rhodium. Rhodium is slowly soluble in hot, concentrated sulphuric acid, and the magnitude of the correction will depend largely upon the length of the treatment of the insoluble residue. Any rhodium going into solution will contaminate the platinum and lead to a high result for that metal.

Results

The analysis of a composite sample of 130 tons of Murray Mine waste rock is given in Table II, the results for gold, platinum, and palladium being given in triplicate and those for iridium and rhodium in duplicate. Silver was not determined on this particular sample, but was calculated to the proportion usually found in Sudbury ores.

TABLE II
ANALYSIS OF MURRAY MINE WASTE ROCK

| Metal | Ounces per ton | | | | Per cent |
|-------------------------|----------------|---------|--------|---------|----------|
| | (1) | (2) | (3) | Av. | |
| Ni | | | | | 0.37 |
| Co | | | | | 0.020 |
| Cu | | | | | 0.335 |
| Ag | | | | 0.030 | |
| Au | 0.0018 | 0.0017 | 0.0019 | 0.0018 | |
| Pt | 0.0038 | 0.0038 | 0.0044 | 0.0040 | |
| Pd | 0.0049 | 0.0055 | 0.0049 | 0.0051 | |
| Ir | 0.00043 | 0.00041 | | 0.00042 | |
| Rh | 0.00060 | 0.00067 | | 0.00063 | |
| Total, Au and Pt metals | | | | 0.01195 | |

It is also of interest to compare the writer's results on this single low-grade sample with those obtained by Beamish and Russell (1) in Sudbury concentrates generally. The agreement, as shown in Table III, is close except in the case of rhodium*, and in view of the use of different methods and the fact that the raw materials merely came from the same general area, may

* Prof. Beamish informs the writer that the iridium and rhodium found by him were not separated, but that the proportions were taken as equal.

TABLE III
RELATIVE PROPORTIONS OF METALS IN ORES OF THE
SUDBURY DISTRICT

| Metal | Beamish and Russell | Lathe |
|-------|---------------------|-------|
| Pt | 37.9 | 33.5 |
| Pd | 42.9 | 42.7 |
| Rh | 2.75 | 5.3 |
| Ir | 2.75 | 3.5 |
| Au | 13.7 | 15.0 |
| | 100.0 | 100.0 |

be termed highly satisfactory. Beamish and Russell made their primary separation by parting the silver bead with sulphuric acid, whereas the writer used the nitric acid method described above.

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ENZYME INHIBITION BY DERIVATIVES OF PHENOTHIAZINE AND OF SULPHANILAMIDE¹

BY H. B. COLLIER²

Abstract

Mammalian catalase and cytochrome oxidase are strongly inhibited by the hydroxy derivatives of phenothiazine and by *p*-hydroxylaminobenzenesulphonamide. Phenothiazine, sulphanilamide, and sulphapyridine have little or no effect. Cytochrome-c is irreversibly reduced by the hydroxy-sulphanilamide, as indicated by spectroscopic observation. The inhibitory activity apparently depends on the presence of the hydroxyl group. The relation of these findings to the vermicial and bactericidal action of the compounds is discussed.

Phenothiazine and thionol have no effect on *Ascaris lumbricoides in vitro*.

Phenothiazine was proposed as an insecticide by Smith, Munger, and Siegler (23) in 1935 and its anthelmintic properties were first described by Harwood, Jerstad, and Swanson (10) and by Swales (24). It has also been demonstrated by DeEds and co-workers (7) that the urine of treated animals is bactericidal. (For formulae of phenothiazine and derivatives see DeEds, Eddy, and Thomas (6).)

The present paper describes an attempt to discover the mechanism of the lethal action of these compounds and to relate this action to their chemical structure. Sulphanilamide and derivatives were also investigated, since it appeared that the two groups of compounds might have analogous properties. This work was based on the hypothesis that chemotherapeutic agents probably act on enzyme systems of the organism, and it was decided that preliminary experiments should be carried out *in vitro* rather than upon actual organisms, where conditions are more complicated and the results more difficult to interpret. As Shinn, Main, and Mellon (22) have suggested that sulphanilamide or its derivatives may inhibit catalase,* an investigation of the hemin catalysts seemed most promising.

Experimental

Phenothiazone and thionol were prepared by the methods of Pummerer and Gassner (17) and of DeEds and Eddy (5), respectively. Each was reprecipitated once from hot water. The leuco derivatives were prepared by reduction of the aqueous solution with ammonium sulphide, extraction with chloroform, drying, and recrystallizing from carbon tetrachloride. Leuco phenothiazone was also isolated from the urinary conjugate excreted by sheep, as previously described (4). Hydroxy-sulphanilamide (*p*-hydroxylaminobenzenesulphonamide, m.p. 140° C.) was obtained through the kindness of Dr. S. M. Rosenthal, of the National Institute of Health, Washington.

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Contribution from the Institute of Parasitology, McGill University, Macdonald College, Que., with financial assistance from the National Research Council of Canada.

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* The term "anti-catalase" is best reserved for the immunological antibody, "catalase inhibitor" being preferable.

Catalase Inhibition

A crude catalase preparation was made from guinea-pig liver by the method of Zeile and Hellström (25). The liver was minced, extracted with water for one hour and filtered. To 100 ml. of the extract was added 50 ml. of 95% ethanol, and the precipitated protein was centrifuged off. To the supernatant fluid was added one-third of its volume of alcohol and 50 ml. of chloroform. After shaking to precipitate the haemoglobin, and filtering, the extract was preserved in the refrigerator.

Catalase activity was measured as follows. To 10 ml. of 1% hydrogen peroxide in 0.02 *M* phosphate buffer, pH 7 (the buffer must not be preserved with thymol, which inhibits catalase), was added 0.2 ml. of enzyme extract. The solution was poured into a graduated fermentation tube and allowed to stand one hour at room temperature, when the volume of oxygen produced was noted. No gas was formed in control tubes with boiled enzyme. A standard curve was prepared, relating enzyme concentration to oxygen volume, since the relation is not linear. This method is crude and only roughly quantitative, but comparable results may be obtained when a number of tests are run simultaneously, under identical conditions of temperature and atmospheric pressure.

Of the compound to be tested for inhibitory power, 1 mg. was added to 0.2 ml. of the enzyme, diluted to 1.0 ml. with buffer. After standing 30 min. at room temperature, enzyme and substrate were mixed, and the determination carried out as described above. Treated and untreated enzyme were compared simultaneously and the degree of inhibition was estimated. In the testing of the leuco compounds the tubes were kept in the dark, to minimize oxidation; the tests on hydroxy-sulphanilamide were carried out in the refrigerator at about 8° C. In every case the degree of oxidation was very slight—insufficient to account for the observed deficit of oxygen production. The results thus obtained with a number of compounds are recorded in Table I.

It is seen that phenothiazine itself has no effect, whereas the derivatives possessing phenolic hydroxyl groups are all strong inhibitors, more effective than phenol itself. Phenothiazone, which contains no hydroxyl group, does

TABLE I
INHIBITION OF LIVER CATALASE

| Compound | Per cent inhibition | Compound | Per cent inhibition |
|---------------------------------------|---------------------|------------------------|---------------------|
| Phenothiazine | 0 | Hexylresorcinol | 100 |
| Leuco phenothiazone | 100 | Phenol | 55 |
| Phenothiazone | 0 | Hydroquinone | 33 |
| Leuco thionol | 100 | Tyrosine | 0 |
| Thionol | 100 | Sulphanilamide | 0 |
| Leuco derivative from urine | 100 | Hydroxy-sulphanilamide | 95 |
| Leuco derivative oxidized by aeration | 0 | Sulphapyridine | 15 |

not inhibit catalase; nor does the leuco derivative from sheep urine, when oxidized by aeration in alkaline solution. This offers further support for the belief that the compound excreted in the urine of sheep as an ethereal sulphate is leuco phenothiazone rather than leuco thionol (4). (However, oxidation with hydrogen peroxide gives a red compound that inhibits the enzyme; this suggests that the oxidation has been carried to the thionol stage.)

Tyrosine apparently does not behave as a typical phenol. It has no effect on catalase, nor does it give a colour reaction with ferric chloride, as do phenolic compounds.

It is of great interest that sulphanilamide itself shows no activity, whereas the hydroxy derivative is a very strong inhibitor. All the substances that inhibited catalase reduced Folin's phenol reagent. Hydroxy-sulphanilamide gave a green colour with ferric chloride, whereas sulphanilamide and sulphapyridine gave no reaction.

Cytochrome Oxidase Inhibition

Cytochrome oxidase (indophenol oxidase) was prepared from beef heart by the method of Keilin and Hartree (12). The preparation oxidized *p*-phenylenediamine without addition of cytochrome-c, and the activity was measured by the method of Battelli and Stern (1), based on this reaction. The enzyme activity was completely destroyed by boiling and by cyanide. The inhibitory effect of the various compounds was determined as follows. One milligram of the substance was added to 0.2 ml. of enzyme and allowed to stand 30 min. at room temperature. To this was added 5 ml. of 0.1% *p*-phenylenediamine in 0.04 *M* phosphate, pH 7.3. After one hour at 37° C. a 1-ml. sample was pipetted into 9 ml. of acetone and centrifuged. The intensity of the red colour was estimated in a photoelectric colorimeter, using a green filter. Colour intensity was found to be directly proportional to enzyme concentration, within the range employed.

Enzyme activity was compared with that of untreated enzyme, determined simultaneously, and the degree of inhibition calculated. Control values with boiled enzyme were allowed for in every case, and it was demonstrated that the inhibitors had no effect on the red pigment produced by oxidation of the substrate. The results obtained with a few compounds are given in Table II; they parallel those obtained with catalase.

TABLE II
INHIBITION OF CYTOCHROME OXIDASE

| Compound | Per cent inhibition | Compound | Per cent inhibition |
|---------------------|---------------------|------------------------|---------------------|
| Leuco phenothiazone | 73 | Sulphanilamide | 0 |
| Phenothiazone | 0 | Hydroxy-sulphanilamide | 100 |
| Thionol | 76 | Sulphapyridine | 0 |

Effect on Cytochrome Absorption Spectrum

Cytochrome-c was prepared from beef heart by the method of Keilin and Hartree (11). Its absorption spectrum was observed visually by means of a Hilger constant deviation spectrometer, through the co-operation of Prof. W. Rowles of the Physics Department, Macdonald College. The solution showed the typical diffuse absorption band of oxidized cytochrome at 520 to 530 m μ . Addition of a trace of hydroxy-sulphanilamide resulted in the appearance of intense bands of reduced cytochrome-c at 550 and 520 m μ . These bands did not disappear on prolonged aeration; this indicated that the pigment had been irreversibly reduced, an effect identical with that obtained with cyanide.

Addition of leuco phenothiazine also caused the appearance of the spectrum of reduced cytochrome-c, but the red colour formed on aeration prevented further observation of the absorption bands.

Anthelmintic Tests in Vitro

The method of Lamson and Brown (13) was used to test the effect, *in vitro*, of phenothiazine and of thionol on *Ascaris lumbricoides*. Five worms were immersed in a 0.1% suspension of phenothiazine in normal saline containing a little bile salts, and an equal number in a saturated solution of thionol in saline. None were killed after exposures up to 24 hr. at 37° C.; by comparison, hexylresorcinol killed within a few minutes.

Discussion

It has been demonstrated that the oxidation products of phenothiazine—leuco phenothiazine, leuco thionol, thionol—strongly inhibit mammalian catalase and the cytochrome oxidase system. The same effect is given by *p*-hydroxylaminobenzenesulphonamide, whereas sulphanilamide itself and sulphapyridine show little or no effect.

It is interesting to speculate whether these findings may not offer an explanation of the vermifugal and bactericidal properties of these compounds. That is, they may act by inhibiting cell respiration, exactly as does cyanide. Nevertheless, because the investigation has been limited to certain mammalian enzyme systems *in vitro*, the results can be used only with caution to explain the effects of the drugs on parasites and bacteria. For example, MacLeod (14) has found that sulphapyridine affects certain dehydrogenases of *pneumococci*; these enzymes are not cytochrome-linked, and are apparently inhibited by a different mechanism from that described above. For this reason, no attempt has been made to review in detail the literature on the mode of action of sulphanilamide.*

The inhibition of the haemin catalysts offers a reasonable explanation of the vermifugal and bactericidal action of the phenolic compounds, and the

* The recent paper of D. D. Woods (*Brit. J. Exp. Path.* 21 : 74-90, 1940) appears to be the best contribution to this problem. He suggests that sulphanilamide may act by competing with aminobenzoic acid, an essential metabolite for certain micro-organisms.

same property (including combination with haemoglobin) is probably responsible for the toxicity of the sulphonamide derivatives, if not for their therapeutic effect. In this connection it is of interest to note that Rimington and Hemmings (18) have observed that the porphyrinuria parallels the toxicity of these compounds, but not their therapeutic action.

Having established that certain compounds produce definite biological effects, it is of great interest to try to correlate chemical structure with these effects. These observations upon the haemin catalysts form a basis for such an attempt. It has been known for some time that phenolic compounds are vermifugal (3, pp. 198-200) and bactericidal; the phenothiazine derivatives fall into this class. It is of great significance that the hydroxylamino derivative of sulphanilamide shows similar properties toward the enzyme systems studied. (It is not a phenol, but it is well known that *enolic* compounds resemble phenols in many respects.) Mayer (16) originally suggested that some such oxidation derivative of sulphanilamide was the active agent, and James (8) has recently isolated such compounds from the urine of treated patients; Scudi (20) has detected hydroxy-sulphapyridine in the urine after administration of sulphapyridine.

Our knowledge of the haemin catalysts leads us to expect that they will be inhibited by such compounds. Sevag and Maiweg (21) and Blaschko (2) have shown that catalase is inhibited by phenols, oximes, and amino derivatives which may give rise to HONH- groups on oxidation. Further, it is these compounds that produce methaemoglobin from haemoglobin, as demonstrated by Sevag and Maiweg, by Harris (9), and by Rimington and Hemmings (18). They reduce Folin's phenol reagent, give a colour reaction with ferric chloride, and their resemblance to the anti-oxidants is worthy of note. Possibly these compounds form complexes with iron and therefore produce the cyanide type of inhibition; or their "anti-oxidant" properties may be more non-specific.

The toxicity of the sulphonamide drugs has been related to their ability to convert haemoglobin to methaemoglobin. Phenothiazine may be given in enormous doses with relatively little host toxicity; the explanation may be that its derivatives in the blood stream, as found in sheep (4), do not penetrate into the erythrocyte. In discussing mechanisms in chemotherapy, this physical factor of permeability may be just as important as the chemical factor of toxicity, and may explain much of the specificity that these drugs seem to exhibit.

As suggested above, the inhibition of the haemin catalysts by the phenothiazine and sulphanilamide derivatives appears to depend on the presence of the hydroxyl group, whether phenolic or enolic. Nevertheless, the activity of these compounds may not reside solely in the hydroxyl group, for they are much more active than phenol itself. As Marshall (15) has pointed out in his review of the pharmacology of sulphanilamide, the newer bactericides all contain sulphur, with a nitro or amino group in the *para* position. Rosenthal (19) states that nitrogen is not essential and that sulphur may be replaced

by arsenic. It seems probable that these atoms serve to increase the polarity of the molecule, thus intensifying the reactivity of the active group. However, it is clear that a satisfactory explanation of the activity of the chemotherapeutic compounds must await a more adequate experimental basis.

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THE KINETICS OF THE DECOMPOSITION REACTIONS OF THE LOWER PARAFFINS

VII. THE NITRIC OXIDE INHIBITED DECOMPOSITION OF ETHANE¹

By E. W. R. STEACIE² AND GERALD SHANE³

Abstract

An investigation has been made of the nitric oxide inhibited thermal decomposition of ethane. Apparent chain lengths of 2.4 to 5 are found at temperatures from 640° to 565° C. The activation energy of the inhibited reaction is found to be 77.3 Kcal. The results are discussed and it is concluded that the thermal decomposition of ethane proceeds mainly by a rearrangement mechanism and that free-radical chain mechanisms for the ethane decomposition are untenable.

Introduction

In the previous paper of this series (6) an investigation of the thermal decomposition of ethane was reported. The activation energy of the reaction was found to be 69.7 Kcal., and it was concluded that the results cast some doubt on the Rice-Herzfeld mechanism for the decomposition (4), and its modification by K  chler and Theile (3). It appeared that further information might be obtained by an investigation of the inhibited reaction.

The inhibition of the decomposition of several of the lower hydrocarbons by nitric oxide has been reported by various workers. Staveley (5) and later Hobbs and Hinshelwood (2) found marked inhibition by small amounts of nitric oxide in the thermal decomposition of ethane at 600° C. Their results indicated a shortening of the chain length with increased ethane pressure. Gray, Travers, and White (1), on the other hand, claimed that the retardation of the rate was due to complex formation between the ethane and nitric oxide, rather than to a chain breaking process.

On the basis of the inhibition of the decomposition by nitric oxide we have evidence of some chain processes in the reaction. The chain lengths measured by this method are, of course, mean chain lengths: the problem whether the chain process proceeds by a very large number of short chains, or by comparatively few very long chains, may possibly be elucidated by further investigation.

Staveley found the activation energy of the fully inhibited reaction to be 74.5 Kcal., which is considerably higher than the value for the normal reaction reported in our previous paper (6). It is, of course, obvious that, if the reaction goes chiefly by a free-radical chain mechanism, with either short or long chains, complete suppression of the chains would give a direct measure of the

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C-C bond strength, since under these conditions the free radical split would become the rate determining step. A comparison of the products of the normal and inhibited reactions should also throw light on the mechanism of the chain process.

Experimental

The apparatus and experimental procedure were exactly the same as those previously employed (6). The results should therefore be strictly comparable.

Nitric oxide was generated by the nitrometer method. The resulting gas was then passed over phosphorus pentoxide and through a trap at -80°C . into a storage reservoir.

The decomposition was investigated at temperatures from 565° to 640°C ., and pressures between 5 and 70 cm. The amount of nitric oxide used corresponded to 1% of the ethane-nitric oxide mixture in all cases, since preliminary runs had indicated maximum inhibition at this concentration.

Results

The greatest inhibitory effect was found during the initial stages of each run. At higher temperatures the inhibition was very transitory, and at 640°C . there was little effect. Towards the later stages of an individual run the rate approaches that of the corresponding uninhibited experiment, as shown by Fig. 1.

The data for a pair of typical runs are given in Table I.

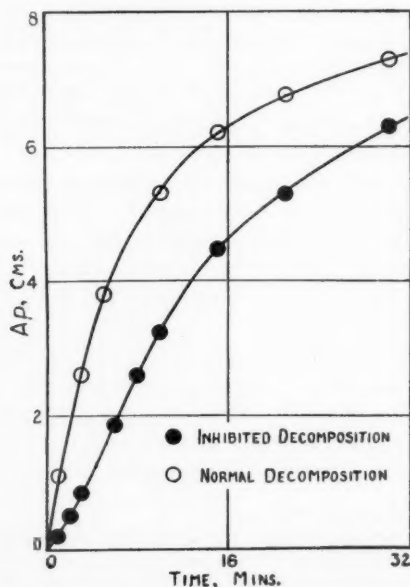


FIG. 1. Comparison of normal and inhibited reaction at 607°C .

TABLE I
DATA FOR TYPICAL RUNS AT 607° C.
Initial ethane pressure—33.0 cm.

| Time, min. | Normal decomposition | | Inhibited decomposition | |
|------------|----------------------|--------------------------------------|-------------------------|--------------------------------------|
| | ΔP , cm. | $K \times 10^6$, sec. ⁻¹ | ΔP , cm. | $K \times 10^6$, sec. ⁻¹ |
| 0 | 0.00 | — | 0.00 | — |
| 1 | 1.10 | 55.5 | 0.22 | 6.06 |
| 2 | 2.00 | 50.5 | 0.52 | 13.1 |
| 3 | 2.60 | 43.7 | 0.85 | 14.3 |
| 5 | 3.80 | 38.4 | — | — |
| 6 | — | — | 1.88 | 15.8 |
| 8 | — | — | 2.58 | 16.3 |
| 10 | 5.30 | 26.8 | 3.20 | 16.2 |
| 15 | 6.20 | 20.8 | 4.46 | 15.0 |
| 21 | 6.75 | 16.3 | 5.28 | 12.7 |
| 30 | 7.30 | 12.3 | 6.28 | 10.6 |

About 150 runs were made on the inhibited reaction. Representative rate data (obtained by taking the tangents to the rate curves at the origin) are given in Table II. As in the normal decomposition the spread in the rate

TABLE II
INITIAL RATE CONSTANTS OF THE INHIBITED REACTION

| Temperature, °C. | Initial pressure, cm. | $K \times 10^4$, sec. ⁻¹ | Temperature, °C. | Initial pressure, cm. | $K \times 10^4$, sec. ⁻¹ |
|------------------|-----------------------|--------------------------------------|------------------|-----------------------|--------------------------------------|
| 565 | 45.7 | 0.14 | 607 | 40.3 | 1.16 |
| | 34.8 | 0.13 | | 28.9 | 1.27 |
| | 31.3 | 0.13 | | 19.3 | 1.07 |
| 572 | 47.7 | 0.21 | 616 | 54.7 | 2.20 |
| | 38.1 | 0.20 | | 43.1 | 2.20 |
| | 37.5 | 0.23 | | 42.9 | 2.02 |
| 580 | — | — | | 41.7 | 2.13 |
| | 59.1 | 0.29 | | 38.8 | 2.23 |
| | 51.0 | 0.34 | | 31.4 | 2.02 |
| | 50.9 | 0.33 | | 23.4 | 2.14 |
| | 42.5 | 0.31 | | 19.7 | 2.06 |
| | 40.1 | 0.33 | 625 | 51.3 | 3.83 |
| 595 | 29.5 | 0.34 | | 47.8 | 3.25 |
| | 54.4 | 0.74 | | 41.7 | 3.90 |
| | 43.5 | 0.73 | | 34.1 | 3.06 |
| | 41.6 | 0.68 | | 25.8 | 3.34 |
| | 39.3 | 0.71 | | 25.3 | 3.70 |
| | 34.7 | 0.70 | | 21.7 | 3.91 |
| | 28.9 | 0.73 | 640 | 50.8 | 7.13 |
| 607 | 54.4 | 1.17 | | 39.5 | 7.41 |
| | 49.1 | 1.19 | | 38.2 | 7.85 |
| | 47.2 | 1.31 | | 36.4 | 8.23 |
| | 41.2 | 1.27 | | 34.9 | 8.28 |
| | | | | 31.2 | 7.26 |

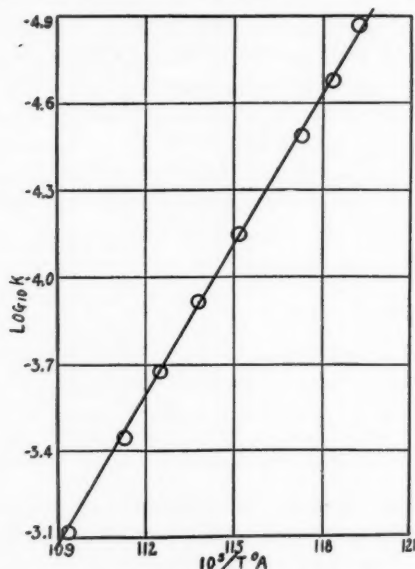


FIG. 2. The temperature coefficient of the inhibited reaction.

constants is comparatively large, again owing to the fact that equilibrium corresponds to only a few per cent decomposition. However, a large number of runs were made and the average values of the rate constants should be quite reliable.

Over the pressure range studied here there is no definite evidence of a falling-off in rate with decreasing pressure. A falling-off of inhibition with rising temperature is noticeable, as expected. The chain lengths found here are in good agreement with those of other workers. The decrease in chain length with rising temperature is shown in Table III. The apparent chain lengths have been calculated in the usual way by taking the ratio of the normal to the inhibited rate. The values of the normal rate constants used for this purpose have been taken from the preceding paper in this series (6).

TABLE III
MEAN APPARENT CHAIN LENGTHS

| Temperature, °C. | Mean apparent chain length | Temperature, °C. | Mean apparent chain length |
|---------------------|-------------------------------|---------------------|-------------------------------|
| 565 | 5.0 | 607 | 3.7 |
| 572 | 4.1 | 616 | 3.4 |
| 580 | 4.0 | 625 | 3.0 |
| 595 | 3.9 | 640 | 2.4 |

In Table IV the mean values of the velocity constants for the inhibited reaction are summarized. These values have been obtained by averaging the initial rate constants from all high pressure runs.

TABLE IV
MEAN VALUES OF INITIAL HIGH PRESSURE RATE CONSTANTS FOR THE INHIBITED REACTION C

| Temperature, °C. | K , sec. ⁻¹ | Temperature, °C. | K , sec. ⁻¹ |
|---------------------|--------------------------|---------------------|--------------------------|
| 565 | 1.34×10^{-4} | 607 | 1.21×10^{-4} |
| 572 | 2.17×10^{-4} | 616 | 2.13×10^{-4} |
| 580 | 3.25×10^{-4} | 625 | 3.57×10^{-4} |
| 595 | 7.13×10^{-4} | 640 | 7.69×10^{-4} |

The values in Table IV are shown in Fig. 2 in the form of a $\log_{10} K - 1/T$ plot. From the slope of the line an activation energy of 77.3 Kcal. is obtained. We thus get

$$\log_{10} K = 15.38 - \frac{77300}{2.3RT} \text{ sec.}^{-1}$$

for the inhibited reaction, as compared with

$$\log_{10} K = 14.02 - \frac{68700}{2.3RT} \text{ sec.}^{-1}$$

for the normal reaction.

TABLE V
ANALYSES AT 595° C.

| Per cent decomposition calculated from pressure increase | Initial pressure, cm. | Moles hydrogen found per mole of ethylene | Ratio of pressure increase calculated from H_2 and C_2H_4 formed to that observed |
|--|-----------------------|---|---|
| 50 | 54.5 | 1.00 | 1.19 |
| 50 | 27.0 | 0.99 | 0.96 |
| 25 | 52.3 | 0.98 | 0.94 |
| 25 | 51.3 | 0.94 | 1.08 |
| 25 | 40.5 | 0.96 | 0.98 |
| 25 | 39.5 | 1.06 | 0.95 |
| 25 | 26.4 | 1.03 | 0.93 |
| 25 | 22.4 | 1.10 | 0.96 |
| 25 | 19.6 | 1.13 | 0.83 |
| 12.5 | 28.9 | 0.92 | 1.09 |

A large number of analyses were made with the object of finding any variation in products with temperature, initial pressure, or per cent decomposition. In addition to hydrogen and ethylene, a small amount of methane was found, which corresponded to from 2 to 5% of the hydrogen. As the equilibrium

corresponds to only 10 to 20% dissociation, in analyses at t_{25} , there will be only 2 to 5% of hydrogen present, so that the actual amount of methane present is very small, and its accurate determination is impossible.

Results of analyses for hydrogen and ethylene at one temperature are given in Table V. It will be seen that, within the rather large experimental error, the hydrogen and ethylene are equal. The pressure increase observed agrees to within the experimental error with that calculated from the hydrogen and ethylene formed. The amount of condensable products formed was not appreciable. Similar results were obtained at other temperatures. A comparison of these results with those for the normal reaction shows that no noticeable difference in the products is brought about by inhibition.

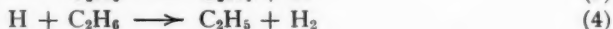
Discussion

The activation energy found here for the nitric oxide inhibited reaction is in fairly good agreement with the value found by Staveley (74.5 Kcal.). The evidence, therefore, points strongly to a value for the activation energy several Kcal. larger than that of the normal reaction; this arises, of course, from the fact that the apparent chain length falls off with rising temperature. The actual chain lengths found here are in excellent agreement with those of Hobbs and Hinshelwood, although they are considerably shorter than those reported by Staveley.

It may be noted that in the present work a much larger reaction vessel was used than was the case in the investigation of Hobbs and Hinshelwood. Since the apparent chain lengths of the two investigations are in good agreement in spite of the large change in surface volume ratio, surface effects apparently play an unimportant part in the inhibition process.

The actual mean chain lengths found here, as pointed out earlier, do not settle the question as to whether short or long chains are involved. We can, however, draw certain conclusions.

In the first place, if we consider the reaction to take place exclusively by a free radical mechanism it is difficult to account for the products of the reaction. In the normal reaction the amount of methane formed is only 2 to 5% of the hydrogen produced. If we attempt a free radical mechanism such as that of Rice and Herzfeld



etc.,

we cannot account for the small values of the methane production unless the chain length is about 50. This is incompatible with our results. Moreover, we would expect a very large increase in methane production when the reaction is inhibited, and this is not found.

It therefore appears that the reaction must proceed by a mixed molecular rearrangement and free-radical mechanism. If this consisted of a small

number of long chains, the products of the reaction could be accounted for. The most likely conclusion, however, appears to be that the reaction proceeds by a mixed radical-rearrangement mechanism, that the reaction chains are short, and that most of the methane formed is due to a side reaction and not to the free radical process.

A remote possibility is that we have a short energy chain of some sort, which can be broken by nitric oxide. This, however, seems to be very unlikely since the mechanism of the inhibition by nitric oxide in various other reactions is undoubtedly the breaking of material chains.

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NITROXYL PERCHLORATE¹

By W. E. GORDON² AND J. W. T. SPINKS³

Abstract

A method for the preparation of nitroxyl perchlorate is outlined. Its empirical formula is NClO_4 . Some of its physical and chemical properties are described.

Introduction

While preparing dichlorine hexoxide by the interaction of chlorine dioxide and ozone (Cf. (6)), the authors observed that a white crystalline substance appeared in the reaction chamber. This crystalline substance was at first assumed to be perchloric acid monohydrate, but it was soon found that this assumption was incorrect. For example, on exposure to the atmosphere the compound decomposed rapidly, forming a white mist. On further investigation, a leak in the oxygen line was discovered through which air was entering the ozonizer. This suggested that oxides of nitrogen might be taking part in the reaction leading to the formation of the compound, and, in fact, tests showed that the compound contained nitrogen. The empirical formula of the compound was subsequently shown to be NClO_4 , and the compound is named nitroxyl perchlorate or nitryl perchlorate.

A search of the literature failed to reveal any previous evidence for the existence of this compound, although somewhat similar compounds have been studied by Hantzsch and his co-workers (7, 8). Hantzsch found that when dry nitric and perchloric acids were mixed in different proportions, two different compounds were formed which corresponded to the addition of one molecule of nitric acid to one and two molecules, respectively, of perchloric acid. They were called nitracidium perchlorate and hydro-nitracidium perchlorate, and assigned the formulae $(\text{O}:\text{N}(\text{OH})_2)^+(\text{ClO}_4)^-$ and $(\text{N}(\text{OH})_3)^{++}(\text{ClO}_4)^{-}_2$, respectively.

The present work covers the preparation and analysis of nitroxyl perchlorate. In addition, some of its physical and chemical properties are described.

Preparation of Nitroxyl Perchlorate

The apparatus is illustrated in Fig. 1. Dry air is passed at about twelve litres per hour through a Siemens type ozonizer operating on 60 cycles and 14,000 volts and kept at 0°C . The resulting gases, containing oxides of nitrogen and ozone, are mixed in a suitable reaction chamber with dry chlorine dioxide prepared by Bray's method (4). The flow of chlorine dioxide must

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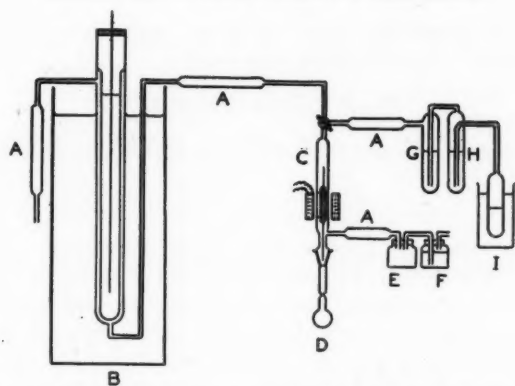


FIG. 1. Apparatus. A, phosphorus pentoxide drying tube; B, Siemen's type ozonizer; C, nitroxyl perchlorate preparation chamber; D, sample bulb; E, trap; F, sodium thiosulphate bubbler; G, sulphuric acid bubbler; H, sodium bicarbonate bubbler; I, chlorine dioxide generator.

be kept small, since, if the flow of chlorine dioxide is rapid, dichlorine hexoxide forms.

A white crystalline compound forms quickly about certain small centres on the walls of the reaction chamber, gradually building out into the interior of the vessel, forming lacy structures. The crystals are loosened from the walls of the vessel by means of a magnetically operated scraper moved up and down inside the vessel by means of a solenoid. The reaction chamber is about 10 cm. long and 1.5 cm. in diameter. The bulb for collection of the sample is blown from 10 mm. glass tubing, with only a slight constriction for the seal-off. A 0.1 gm. sample of the compound can be prepared in about an hour.

Qualitative Analysis

The substance reacted with water, yielding an acid solution that gave negative tests for Cl^- , ClO_3^- and NO_2^- . Positive tests were obtained for NO_3^- and ClO_4^- . The tests, with the exception of the microscopic ones, were carried out according to directions in Treadwell and Hall's "Analytical Chemistry", Vol. 1.

1. Silver nitrate test for chlorides—negative.
2. Sulphur-dioxide-silver-nitrate test for chlorates—negative.
3. Ferrous-sulphate-silver-nitrate test for chlorates—negative.
4. Potassium permanganate test for nitrites—negative.
5. Brown ring test for nitrates—positive.
6. Tests under the microscope with potassium chloride solution and also with 2% brucine solution for perchlorates—positive.

It thus appeared that the substance reacted with water to form nitric and perchloric acids only and should, therefore, be regarded as a mixed anhydride of these acids of empirical formula, NClO_6 . Subsequent analyses have confirmed this conclusion.

The absence of a reaction with potassium permanganate solution rules out the possibility of nitrosyl perchlorate (9, 10).

Quantitative Analysis

The percentages of nitrogen and chlorine and the acid equivalent were next determined.

Nitrogen

This was determined by means of a Lunge nitrometer. A sealed bulb containing a sample of the compound was broken under concentrated sulphuric acid in a cup connected to the nitrometer. The sulphuric acid mixture was drawn into the nitrometer and the cup rinsed with a little water that was also drawn into the nitrometer in the usual way. The volume of nitric oxide was measured after shaking with mercury for about ten minutes. In calculating the volume of nitric oxide under standard conditions, a correction of 6 mm. was made for the vapour pressure of the sulphuric acid solution, which was approximately 50% sulphuric acid in each experiment.

TABLE I
NITROMETER ANALYSES

| Wt. of sample | Volume of NO, cc. | Temp., °C. | Pressure, mm. Hg. | Per cent N |
|---------------|----------------------|---------------|----------------------|---------------|
| 0.1500 | 26.8 | 25 | 722 | 9.64 |
| 0.1885 | 33.4 | 20 | 725 | 9.75 |
| 0.1411 | 24.8 | 20 | 726 | 9.69 |
| | | | | Mean 9.69 |

The calculated percentage of nitrogen in nitroxyl perchlorate is 9.62.

Chlorine

The analysis for chlorine, known from the above qualitative tests to be present as perchlorate, was done on aliquot portions of a solution obtained by dissolving weighed samples in standard sodium carbonate solution. About 1 gm. of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ was added to the aliquot, which was then evaporated to dryness in a platinum dish and heated to a dull red heat. This decomposed the perchlorate to chloride which was then determined by the Volhard method using 0.01 *N* silver nitrate. The percentage chlorine in two experiments, using different samples of the compound, was 24.30 and 24.86. An analysis by the Carius method gave 24.69%. The mean value for the three experiments is 24.62%; this agrees very well with the theoretical (24.35%) for nitroxyl perchlorate.

Acid Equivalent

This was determined by back titrating an aliquot of the solution in standard sodium carbonate solution obtained as above with standard sulphuric acid.

Acid equivalents of 72.40 and 72.52 were obtained; mean = 72.46. The theoretical acid equivalent for nitroxyl perchlorate is 72.77 if one supposes the following reaction to take place with water: $\text{NClO}_6 + \text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{HClO}_4$. The above evidence seems sufficient to assign to the compound an empirical formula NClO_6 , with a formula weight of 145.5 and an acid equivalent of 72.7.

The compound is named nitroxyl perchlorate or nitryl perchlorate.

Physical and Chemical Properties of Nitroxyl Perchlorate

Samples of the compound contained in a thin walled flat glass tube were examined microscopically. The crystals consist of spikelets emerging at different angles from a central needle, the average over-all length of a crystal being less than a millimetre. The crystal habit was not determined.

Preliminary experiments indicate that the compound has a vapour pressure less than 0.05 mm. of mercury at room temperature. It begins to decompose rapidly at 120° C. Nitroxyl perchlorate has not been observed to decompose explosively.

Nitroxyl perchlorate is soluble in phosphorus oxychloride, insoluble in carbon tetrachloride.

As might be expected, nitroxyl perchlorate reacts readily with most organic materials. It reacts with benzene, giving a slight detonation and a flash. Some nitrobenzene is formed.

Sharp detonations, with ignition of the liquid, occurred with acetone and ether.

Rapid reaction, without explosion, occurred with alcohol and glycerol. It is possible that perchloric esters may be produced in these last two reactions (11).

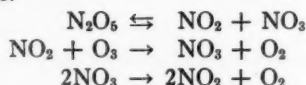
The compound reacted readily with iodine on warming, forming a white solid, iodine pentoxide, and a volatile reddish brown liquid, probably iodine monochloride. The white solid dissolved in water giving an acid solution that gave positive tests for iodate with silver nitrate, barium chloride, and lead acetate solutions. When treated with ferrous sulphate plus dilute sulphuric acid or with potassium iodide solution, iodine was liberated. These tests indicate the presence of iodine pentoxide. A sample of the white solid weighing 0.0227 gm. was analysed quantitatively for iodine pentoxide by dissolving it in a solution of potassium iodide in 0.1 *N* sulphuric acid and titrating the liberated iodine with 0.104 *N* sodium thiosulphate solution; 7.85 cc. of thiosulphate were used, indicating that the white substance was 100% iodine pentoxide.

Discussion of Results

Mechanism of Formation

The probable mechanism for the formation of nitroxyl perchlorate in this reaction will be briefly discussed.

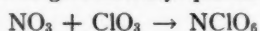
Earlier work has established that the products resulting from the passage of air through a discharge are mainly nitrogen pentoxide and ozone (5, 13, 2). Furthermore, Schumacher and Sprenger (14, 15) and Lowry and Seddon (12) have shown spectroscopically that NO_3 is present in mixtures of nitrogen pentoxide and ozone.



ClO_3 is also present in the reaction chamber, owing to the interaction of chlorine dioxide and ozone. (1, 6).

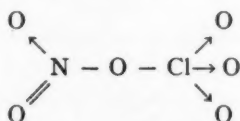


NO_3 and ClO_3 combine to give nitroxyl perchlorate.



Structure

Assuming that the molecular formula is the same as the empirical formula, the authors would suggest as a possible electronic structure for nitroxyl perchlorate:



which would behave as a mixed anhydride of nitric and perchloric acids. Alternatively, the compound may be ionic in character, with the structure $(\text{NO}_2)^+(\text{ClO}_4)^-$. This would be analogous to the structure, $(\text{NO})^+(\text{ClO}_4)^-$, assigned to nitrosyl perchlorate on the basis of conductivity measurements in dry nitromethane and supported by Raman Spectra evidence (8, 9, 3). Further work on nitroxyl perchlorate has been planned.

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THE BROMINE SENSITIZED PHOTODECOMPOSITION OF OZONE¹

BY R. MUNGEN² AND J. W. T. SPINKS³

Abstract

Bromine acts as a sensitizer for the photodecomposition of ozone. The quantum efficiency for the bromine sensitized reaction is about 30. The effect of variation of wave-length, concentration, light intensity, and temperature has been studied. The quantum efficiency is the same for wave-lengths 5460 and 3650 Å and is independent of the ozone concentration, but varies somewhat with bromine concentration and light intensity. The temperature coefficient is 1.01. Under certain conditions an oxide of bromine, produced photochemically, can be isolated.

Introduction

As is well known, the halogens act as catalysts or sensitizers in a large number of thermal and photochemical reactions. A detailed study of these reactions indicates that they can all be explained by chemical mechanisms involving halogen atoms (9, 14).

The decomposition of ozone is catalyzed by both chlorine and bromine. The chlorine catalyzed reaction is now fairly well understood and involves the production of oxides of chlorine as intermediate compounds (14, p. 129).

The present work concerns the photosensitized decomposition of ozone with bromine as the sensitizer.

Gaseous mixtures of ozone and oxygen are quite stable at room temperature but if bromine is added to the mixture, a catalyzed decomposition of the ozone occurs. Elaborate studies of the thermal reaction of ozone and bromine have been carried out by Lewis and Feitknecht (5) and Lewis and Schumacher (6). They suggest that a chain reaction takes place and that an unstable oxide of bromine is formed as an intermediate compound.

The photochemical decomposition of ozone in the presence of bromine has been reported to be a chain reaction with a quantum yield of about 30 (2, 13). The present work extends this earlier work and covers the effect of varying (a) the concentration of both bromine and ozone, (b) the light intensity, (c) the temperature, and (d) the wave-length. Work leading to the isolation of an oxide of bromine, formed photochemically, is also described.

Experimental

Materials and Apparatus

Ozone was prepared from oxygen in a Brodie type ozonizer operating on 60 cycles and 14,000 volts. The oxygen was prepared by the electrolysis of 20% sodium hydroxide between nickel electrodes. The oxygen was freed

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Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Sask. From part of a thesis by R. Mungen in partial fulfilment of the requirements for the degree of Master of Science.

² Holder of a Bursary under the National Research Council of Canada, 1939-40.

³ Professor of Physical Chemistry.

from traces of hydrogen and was thoroughly dried before it passed to the ozonizer. The ozone thus obtained was about 6% by volume. Ozone concentrations up to 85% were obtained by liquefaction of an ozone-oxygen mixture in a liquid air trap followed by pumping to free from oxygen and subsequent vaporization of the relatively pure ozone. It should be mentioned perhaps that the ozone sometimes explodes quite violently while vaporizing and the experimenter should therefore be protected by a sheet of plate glass.

The bromine was of c.p. grade and was dried over phosphorus pentoxide.

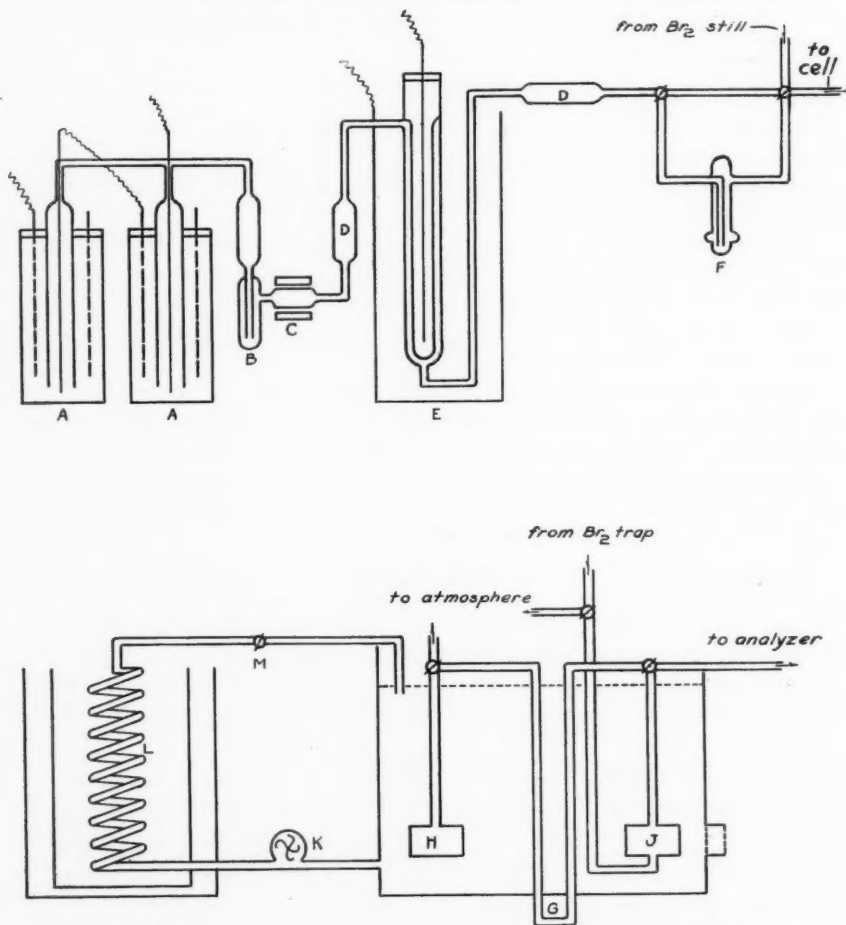


FIG. 1. Apparatus. A, oxygen electrolysis cell; B, sulphuric acid bubbler; C, palladium tube and heater; D, phosphorus pentoxide tube; E, Brodie type ozonizer; F, bromine bubbler; G, sulphuric acid manometer; H, balancing cell; J, reaction cell; K, pump; L, cooling coil; M, tap.

Light Source and Light Filters

A slightly convergent beam of reasonably monochromatic light was obtained from a quartz mercury arc run in conjunction with a voltage regulator and the usual light filters for 5460 and 3650 Å (3, p. 116). Energy measurements were made with a calibrated Moll 2 cm. surface thermopile, connected in series with a moving coil galvanometer, and were checked by experiments on the chlorine-ozone reaction. A scale deflection of 1 mm. of the galvanometer corresponds, at 5460 Å, to 1.99×10^{15} quanta per min.

A low pressure mercury arc was used to obtain the 2537 line, and its intensity was measured actinometrically using 0.5 *N* chloracetic acid (4). The photo reactions were usually performed in flat ended glass cells 10 cm. in length and 5 cm. in diameter, although in some experiments a quartz cell was used.

The reaction $2\text{O}_3 \rightarrow 3\text{O}_2$ takes place with an increase in number of moles. Consequently, the course of the reaction was followed by measuring the pressure change on a capillary sulphuric acid manometer (Fig. 1). Measurements were made with a cathetometer (1, p. 1656).

Bromine was introduced into the reaction cell by bubbling part of the ozone-oxygen mixture through a bromine trap. The percentage of bromine present was determined either by chemical analysis or by measurement of the percentage absorption of light of wave-length 5460 Å.

Atmospheric pressure was used in all experiments.

The temperature of the cells was thermostatically controlled, the usual type of thermostat being used for temperatures between 0° and 30° C. Temperatures down to -80° C. were obtained in a small thermostat containing acetone, cooled by circulation through a cooling coil kept at -80° C. by means of a dry ice-acetone mixture. Frosting of the cell window was prevented by using a double window arrangement (Fig. 2). It will be noticed that, in the low temperature set-up, the bromine trap is also in the thermostat. This arrangement avoids the troublesome deposition of bromine in the reaction cell which might take place if the bromine trap were at a higher temperature than the thermostat.

Results

The course of a typical experiment is illustrated in Fig. 3 (6% ozone, 3% bromine, 5° C., 5460 Å). It will be noticed that there is a small thermal reaction taking place in the dark. When light is shone on the mixture, there is a sudden rise in pressure, the Budde and Draper* effect, which is followed by a uniform rate of increase in pressure due to the sensitized decomposition of the ozone, $2\text{O}_3 \rightarrow 3\text{O}_2$. If at any time the light is cut off, there will be a drop in pressure owing to the inverse Budde and Draper effect. If insolation is continued, the uniform rate of increase of pressure is maintained until all the ozone is decomposed. The uniform rate of increase of pressure is quite typical and indicates that the quantum yield is independent of the ozone concentration.

* For an explanation of these terms see (7, p. 111).

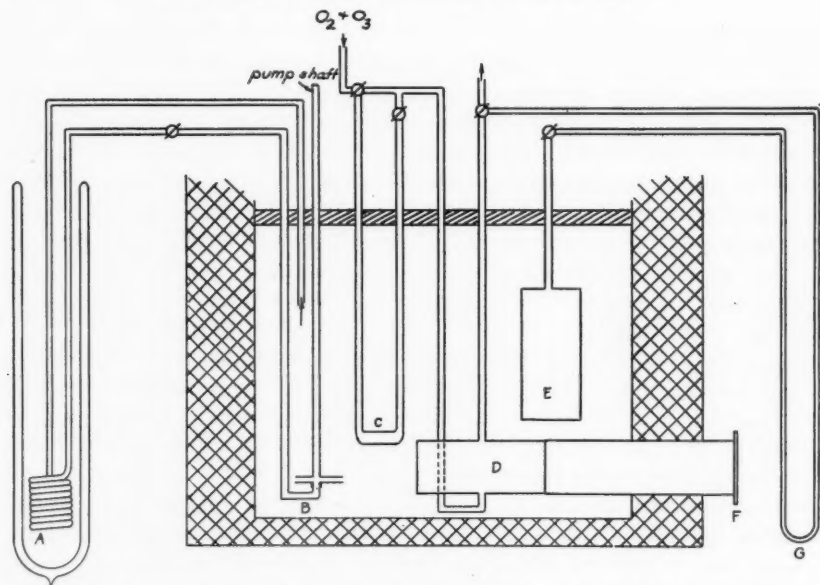


FIG. 2. Low temperature thermostat and apparatus. A, cooling coil; B, pump stirrer; C, bromine trap; D, reaction cell; E, balancing cell; F, window; G, manometer.

In order to keep the thermal reaction small compared to the photo reaction, experiments were done in the neighbourhood of 0°C . Lower temperatures could not conveniently be used owing to the low vapour pressure of bromine below 0°C . The thermal reaction was particularly troublesome in the quartz cell, pointing to a surface action. It was found that the thermal reaction could be very largely suppressed by introducing a small amount of water into the reaction cell. Consequently, a few experiments, mostly those at higher temperature, were done in the presence of moisture.

Quantum Yields

Variation of Concentration of Bromine and Ozone

Quantum yields for 6% ozone and varying proportions of bromine are shown in Table I. The rather low vapour pressure of bromine at 1°C . (70 mm.) prevented the employment of a higher proportion of bromine. It will be noted that the quantum yield is not appreciably affected by the presence of moisture at this temperature.

A large number of experiments have shown that the quantum yield is independent of ozone concentration, up to 12% ozone. Quantum yields could not be measured with ozone concentrations greater than 12% owing to the occurrence of a very rapid thermal reaction. With 20% ozone the situation is still further complicated by the production of a solid oxide of bromine which settles out on the walls (cf. 5, 6).

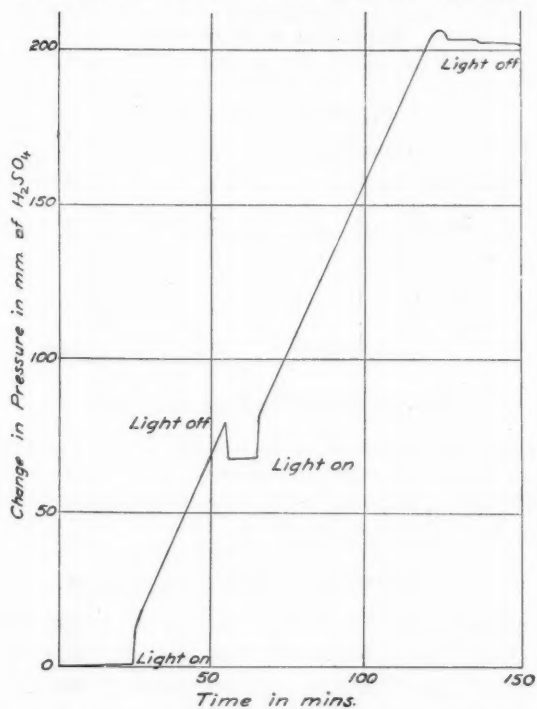


FIG. 3. Graph showing results obtained in a typical experiment—6% ozone, 3% bromine, 5° C., 5460 Å.

TABLE I

QUANTUM YIELDS

Temperature, 1° C.; dry glass cell

| 5460 Å | | 3650 Å | |
|---------------------|------------------------|---------------------|----------|
| Br ₂ , % | γ | Br ₂ , % | γ |
| 1.6 | 31.8 | 2.2 | 25.8 |
| 3.4 | 25.1 | 3.3 | 28.4 |
| 4.3 | 25.4 | 6.5 | 27.4 |
| 5.5 | 26.3 | | |
| 6.1 | 24.6 | | |
| 7.8 | 25.4 | | |
| (2.9) | 27.4 moisture in cell) | | |

The intensity was varied three-fold using a wire gauze screen. In the presence of moisture, the rate was directly proportional to the intensity. However, using dry gases, the quantum yield increased slightly with decreasing intensity. The increase was the greater the lower the percentage of bromine. The results are recorded in Table II. Each ratio in the table is the mean of several experiments.

Variation of Intensity

TABLE II

VARIATION OF INTENSITY

Dry cell: $\lambda 5460 \text{ \AA}$, 5° C. , 6% O_3

| Br_2 , % | Ratio intensities | Ratio rates |
|-------------------|-------------------|-------------|
| 6 - 7 | 0.355 | 0.386 |
| 2 - 3 | 0.355 | 0.402 |
| 0.5 - 1 | 0.355 | 0.443 |

Temperature Coefficient $\lambda 5460 \text{ \AA}$

Quantum yields were measured at 5° and 23° C. for a given mixture, and the temperature coefficient was calculated for a 10 degree change in temperature. With water present in the cell, a temperature coefficient of 1.01 was obtained in five different experiments.

Variation in Wave-length

For a given mixture, quantum yields were determined for 5460 and 3650 \AA and found to be the same, despite the fact that, for bromine, these wave-lengths lie in the regions of discrete and continuous absorption, respectively, e.g., 2% bromine, 6% ozone; 5° C. ;

$$\gamma_{5460} = 23.6, \quad \gamma_{3650} = 23.0.$$

Using a quartz cell and 2537 \AA , quantum yields approaching 7 were obtained (6.5, 6.2, and 6.7 in three different experiments). Owing to the low intensity of 2537 and the fact that the energy measurements had to be made actinometrically, the accuracy of this figure is probably not very great. However, it is certainly much lower than the corresponding figure for 5460 or 3650 \AA . The lowness of the quantum yield is probably related to the fact that, at 2537 \AA , ozone is the light absorbing component. There was no measurable decomposition of the ozone in the absence of bromine at 2537 \AA , presumably owing to the low intensity and the large excess of oxygen present. This agrees with Schumacher's findings (8), who reports quantum yields as low as 0.3 for low concentrations of ozone.

Low Temperature Work and Isolation of a Bromine Oxide

The relatively high quantum yield suggested that unstable bromine oxides might be formed in the course of the photo reaction. After a considerable amount of experimenting, the conditions necessary for the isolation of an oxide were established. Eventually, streaming experiments were performed at -40° C. using 6% ozone and 3 mm. bromine (Fig. 4). After passage of

the gases through the cell for an hour in the dark, there was no indication of oxide formation (the cell and its contents were made visible by the small light *B*), so that evidently an oxide is not formed thermally under these conditions. The gases were then illuminated with light from the mercury arc and in the course of two or three minutes a mist appeared in the cell. Shortly after this, white crystals appeared on the cell walls and continued to accumulate as the gases were streamed through. When the temperature was allowed to rise, the oxide decomposed with formation of bromine and oxygen.

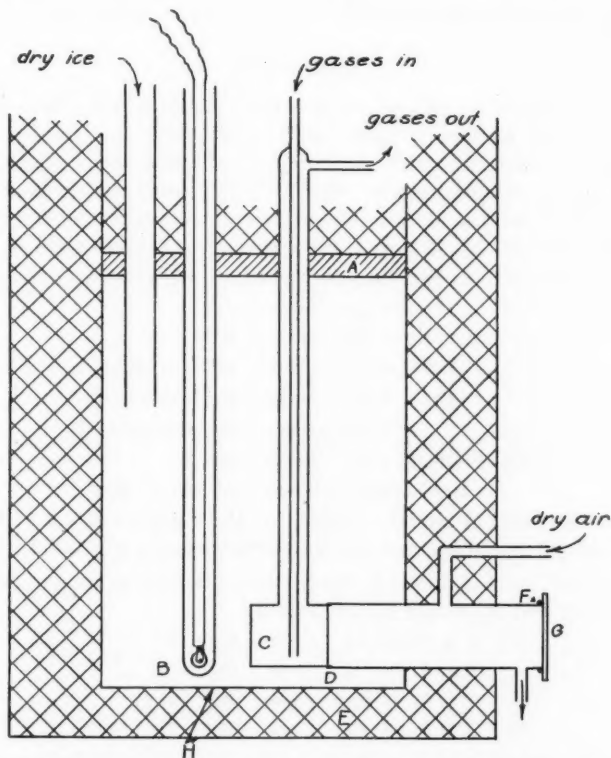


FIG. 4. Apparatus for isolation of oxide of bromine. *A*, cork; *B*, light; *C*, cell; *D*, rubber gasket; *E*, absorbent cotton; *F*, cement; *G*, glass window; *H*, tin containers.

The oxide is very similar in appearance to the white oxide Br_3O_8 , but is different in appearance from Br_2O and BrO_2 , dark brown and light yellow, respectively (10, 11, 12).

When temperatures below -40°C . are tried, the very low vapour pressure of bromine makes the process of oxide formation unduly long; while at higher temperatures the oxide cannot be isolated. On the other hand, if the amount of ozone is much greater than 6%, the formation of the oxide takes place

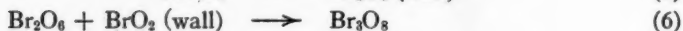
thermally. For example, using 20% ozone and 4 to 8 mm. of bromine, a white deposit of Br_3O_8 was formed in a few minutes at 1°C .

Using 3 mm. of bromine and 6% of ozone and temperatures near -40°C . the oxide could be produced photochemically at will. It was found that wave-lengths of 5460, 3650, and 2537 Å were effective.

Thus far the oxide has not been analysed quantitatively, although a method involving the use of a glass spoon gauge has been shown to be feasible. However, it has been definitely shown that an oxide of bromine, probably Br_3O_8 , is produced photochemically in the bromine-ozone reaction.

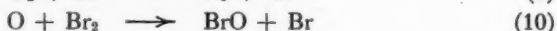
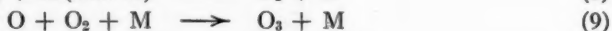
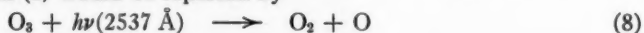
Discussion

A detailed discussion of the reaction must await a fuller knowledge of the properties of the various bromine oxides. However, the present work indicates that the reaction is very similar to the chlorine-ozone photo reaction in many respects. Consequently, the following very tentative mechanism, resembling that for the chlorine-ozone reaction, is suggested for experiments using 5460 and 3650 Å. It accounts for the high quantum yield and the formation of an oxide of bromine but does not make any claim to finality.



Reactions (3) and (4) would account for the high quantum yield and (3), (4), (5), and (6) would account for the production of higher oxides of bromine.

The reaction at 2537 differs in the primary absorption act and consequently Reactions (1) and (2) would be replaced by



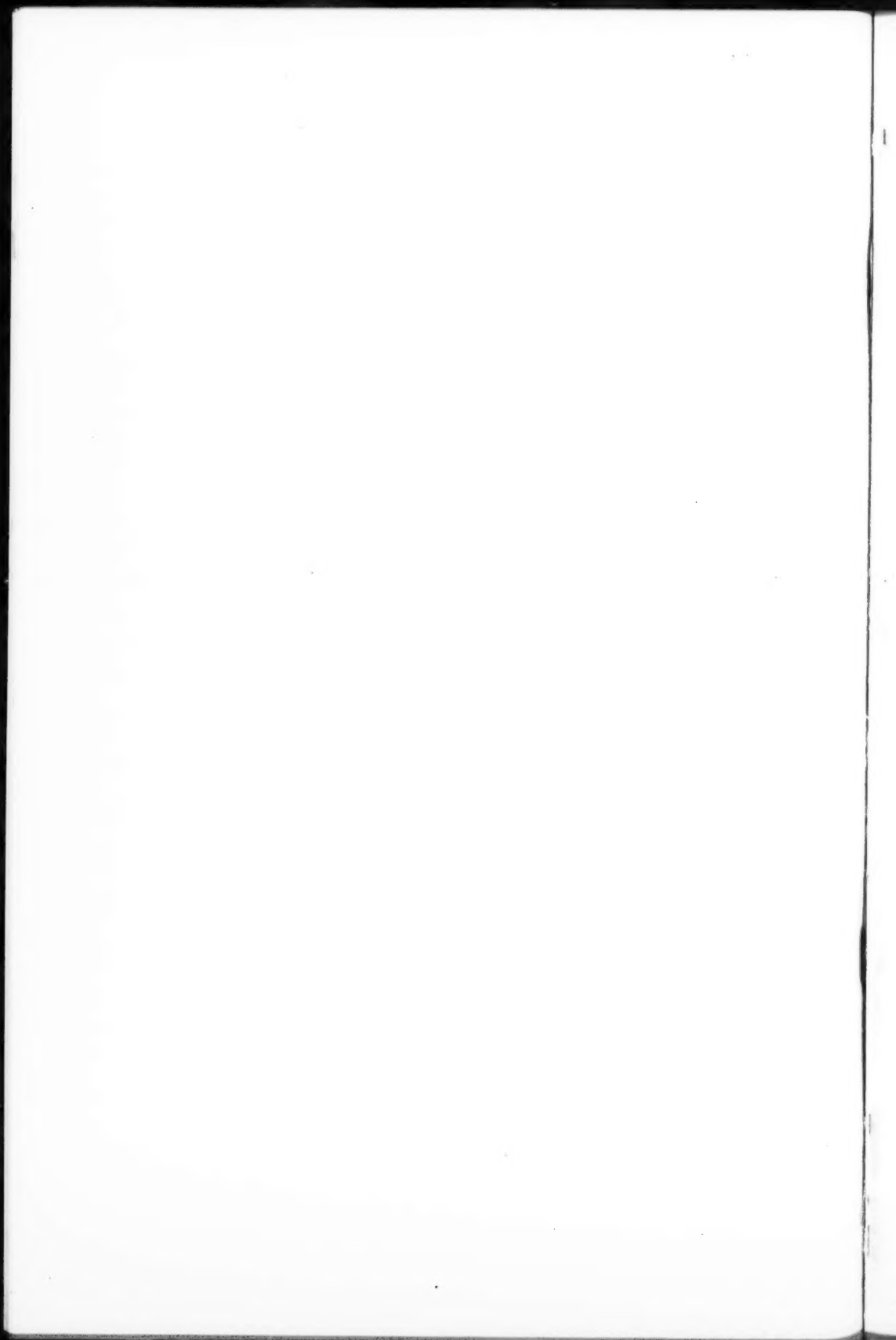
with subsequent reactions as above. M is a triple collision partner; either bromine or ozone. This mechanism would lead to a quantum yield at 2537 Å somewhat less than half that for the bromine sensitized reaction at 5460 and 3650 Å and thus finds some support from experiment.

Further attempts to analyse the oxide of bromine are being made.

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